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Molecular Factors Controlling Photosynthetic Light Harvesting by Carotenoids

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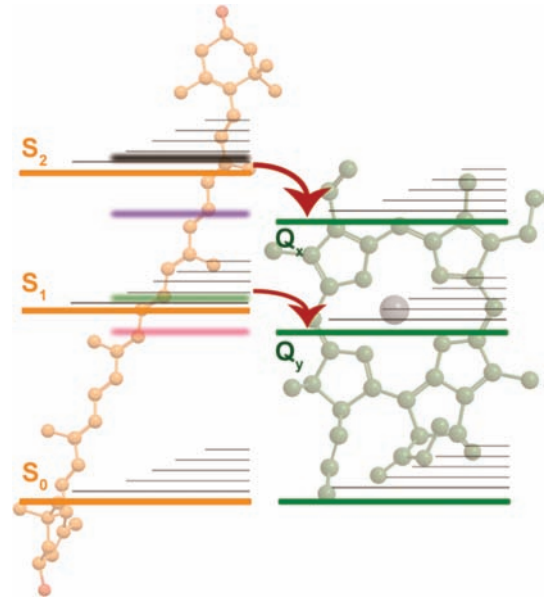

Carotenoids are naturally occurring pigments that absorb light in the spectral region in which the sun irradiates maximally. These molecules transfer this energy to chlorophylls, initiating the primary photochemical events of photosynthesis. Carotenoids also regulate the flow of energy within the photosynthetic apparatus and protect it from photoinduced damage caused by excess light absorption. To carry out these functions in nature, carotenoids are bound in discrete pigment–protein complexes in the proximity of chlorophylls. A few three-dimensional structures of these carotenoid complexes have been determined by X-ray crystallography. Thus, the stage is set for attempting to correlate the structural information with the spectroscopic properties of carotenoids to understand the molecular mechanism(s) of their function in photosynthetic systems.

In this Account, we summarize current spectroscopic data describing the excited state energies and ultrafast dynamics of purified carotenoids in solution and bound in light-harvesting complexes from purple bacteria, marine algae, and green plants. Many of these complexes can be modified using mutagenesis or pigment exchange which facilitates the elucidation of correlations between structure and function. We describe the structural and electronic factors controlling the function of carotenoids as energy donors. We also discuss unresolved issues related to the nature of spectroscopically dark excited states, which could play a role in light harvesting.

To illustrate the interplay between structural determinations and spectroscopic investigations that exemplifies work in the field, we describe the spectroscopic properties of four light-harvesting complexes whose structures have been determined to atomic resolution. The first, the LH2 complex from the purple bacterium *Rhodopseudomonas acidophila*, contains the carotenoid rhodopin glucoside. The second is the LHCII trimeric complex from higher plants which uses the carotenoids lutein, neoxanthin, and violaxanthin to transfer energy to chlorophyll. The third, the peridinin-chlorophyll-protein (PCP) from the dinoflagellate *Amphidinium carterae*, is the only known complex in which the bound carotenoid (peridinin) pigments outnumber the chlorophylls. The last is xanthorhodopsin from the eubacterium *Salinibacter ruber*. This complex contains the carotenoid salinixanthin, which transfers energy to a retinal chromophore. The carotenoids in these pigment–protein complexes transfer energy with high efficiency by optimizing both the distance and orientation of the carotenoid donor and chlorophyll acceptor molecules.

Importantly, the versatility and robustness of carotenoids in these light-harvesting pigment–protein complexes have led to their incorporation in the design and synthesis of nanoscale antenna systems. In these bioinspired systems, researchers are seeking to improve the light capture and use of energy from the solar emission spectrum.

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Introduction

Carotenoids make up a group of natural pigments whose central structural feature is a linear chain of alternating C−C and C=C bonds.[1] They differ in π-electron conjugation length (number of conjugated double bonds, *N*) and in the type and number of functional groups attached to the carbon backbone. Of the more than 1000 naturally occurring carotenoids, only ~50 play a light-harvesting role in photosynthesis. The structures of four such carotenoids are shown in Figure 1.

The ability of carotenoids to act as light-harvesting agents is inextricably linked to their spectroscopic properties which are best described using a three-state model consisting of the ground state, S_0, and two excited states denoted S_1 and S_2 (Figure 1). The symmetry of the fully extended conjugated π-electron backbone places carotenoids in the C_{2h} point group, and a further consideration of the symmetry of the individual π-orbitals assigns the S_0 and S_1 states to the A_g^- irreducible representation. The S_2 state has B_u^+ symmetry. Because one-photon transitions between electronic states of the same symmetry are forbidden by quantum mechanical selection rules, the $S_0 \rightarrow S_1$ transition is forbidden, and the lowest-energy allowed transition is the $S_0 \rightarrow S_2$ transition.[2,3] It should be noted that a few other states into which transitions from S_0 are forbidden may exist either between or in the vicinity of S_2 and S_1, further complicating the carotenoid photophysics.[4] After absorption of light via the $S_0 \rightarrow S_2$ transition, the S_2 state relaxes within a few hundred femtoseconds to the S_1 state whose lifetime depends on *N* and is between 1 and 200 ps for most natural carotenoids.[3]

At first glance, carotenoids are not pigments that one would expect nature to choose as light-harvesting molecules because the lifetimes of the S_1 and S_2 states are significantly shorter than those of other naturally occurring pigments such as (bacterio)chlorophylls (B)Chls; any possible energy transfer route using the S_1 or S_2 state of carotenoids as an energy donor must contend with these very short intrinsic relaxation times. Moreover, a transition between the ground state and the S_1 state is forbidden, resulting in a negligible transition dipole moment, the consequence of which is that the S_1 state cannot participate in Förster-type dipole−dipole-mediated energy transfer. Thus, the subpicosecond lifetime of the S_2 state and negligible dipole moment of the S_1 state would

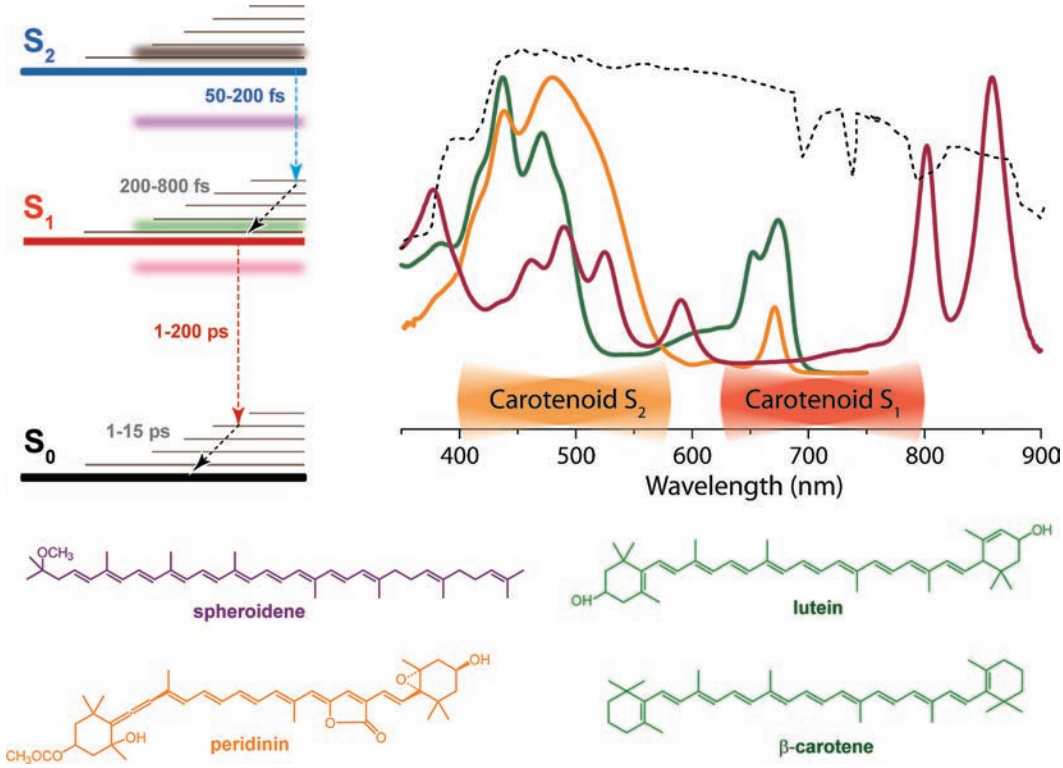

FIGURE 1. Three-state model (top left) of carotenoid excited states consisting of S_2 (blue) and S_1 (red) states. Relaxation processes are denoted by arrows and corresponding time constants. Internal conversion processes are denoted by blue and red arrows; black arrows denote vibrational relaxation. Blurred lines denote the other states whose role in energy transfer is less clear: ICT (red), S* (green), $1^1B_u^-$ (purple), and $3^1A_g^-$ (black). Absorption spectra (top right) of LH2 (purple), PCP (orange), and LHCII (green). The range of energies of carotenoid S_2 and S_1 transitions are also shown by the orange and red bars beneath the spectra. The dashed line denotes the solar irradiance spectrum emphasizing the importance of carotenoids in light harvesting. Molecular structures (bottom) of four important carotenoids. Color coding corresponds to the absorption spectra of the light-harvesting complexes in which they are found.

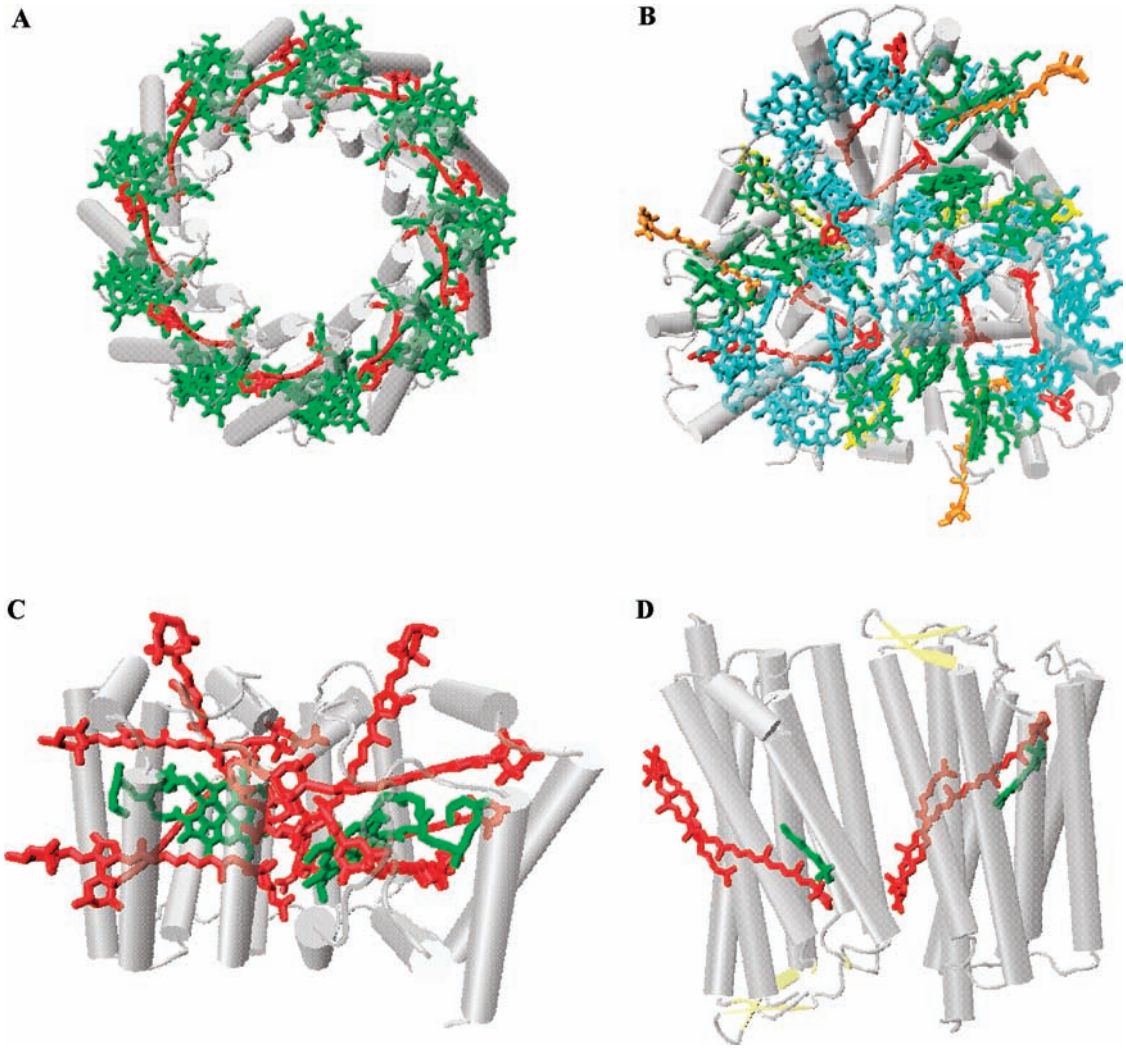

FIGURE 2. Structures of four light-harvesting complexes exhibiting energy transfer from carotenoids. (A) LH2 complex of the purple bacterium *Rhodopseudomonas acidophila* having the carotenoid rhodopin glucoside (red) and BChl-*a* (green). (B) LHCII trimer utilizing the carotenoids lutein (red), neoxanthin (yellow), and violaxanthin (orange) in the transfer of energy to Chl-*a* (blue) and Chl-*b* (green). (C) Peridinin-Chl-*a*-protein from the dinoflagellate *Amphidinium carterae*. Eight peridinin molecules (red) transfer energy to two Chl-*a* molecules (green). (D) Xanthorhodopsin from the eubacteirum *Salinibacter ruber*. The carotenoid salinixanthin (red) transfers energy to the retinal chromophore (green).

appear to hardly qualify carotenoids as effective light-harvesting molecules. However, essentially all photosynthetic organisms utilize carotenoids as light-harvesting pigments, and both the S_1 and S_2 states of carotenoids function as energy donors.

The high efficiency of carotenoid-mediated energy transfer in light-harvesting proteins is achieved by optimization of the distance and orientation of the carotenoid donor and the (B)Chl acceptor. In most light-harvesting proteins, the distance between the conjugated systems of the donor and acceptor is between 3 and 10 Å (Figure 2). Combined with a proper orientation and a large dipole moment of the S_2 state, it was calculated that the S_2-mediated carotenoid-to-(B)Chl energy transfer occurs in 100−300 fs via the Förster mechanism,[5] i.e., clearly competitive with the intrinsic carotenoid S_2 lifetime. However, because the donor−acceptor distance is smaller than dimensions of participating molecules, the donor−acceptor interaction term in the Förster formalism must be calculated using elaborate quantum mechanical methods.[6] Transfer of energy from the carotenoid S_1 state can also be considered to proceed via a Förster mechanism, but because of the dipole-forbidden nature of this state, it is necessary to compute the full Coulomb coupling between the donor and acceptor molecules to achieve reasonable agreement with experiment.[6]

Whether the S_1 or S_2 state acts as the energy donor depends in large part on *N*, because this is a primary factor in determining the energies of the states relative to those of the energy acceptor. Energy transfer according to the Förster

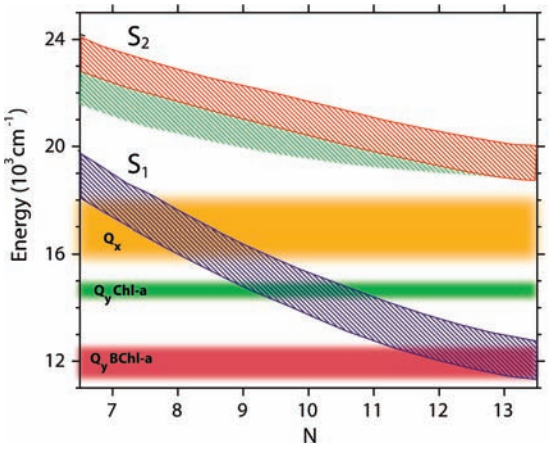

FIGURE 3. Dependence of the S_1 (blue) and S_2 (red) state energies of carotenoids on their number of conjugated double bonds, *N*. The width of the bands corresponds either to the variability in state energy due to the environment or to uncertainty in determining the energy. The green band corresponds to S_2 energies of carbonyl carotenoids. Energies of typical acceptor states are also shown.

mechanism will be optimized when the spectral overlap between the S_1 and/or S_2 donor emission and acceptor absorption is maximized. The *N* dependence of the energies of the S_1 and S_2 states, together with energies of acceptors in various light-harvesting systems, is shown in Figure 3. It is clear from the figure that an energy transfer pathway between the carotenoid S_2 state and Q_x state of (B)Chl is favorable for a broad range of conjugation lengths. Indeed, the S_2-mediated energy transfer operates in almost all carotenoid-containing light-harvesting systems regardless of the conjugation length of the carotenoid. In contrast, the S_1 state can act as an efficient energy donor only if the acceptor has a lower energy, as it does in light-harvesting complexes utilizing BChl-*a*. If the energy acceptor is Chl-*a*, only carotenoids having short π-electron conjugations will be able to use the S_1 pathway. Also, while the S_1 energy is nearly insensitive to the environment, the S_2 energy may be modulated by interaction with proteins. In addition, the effective conjugation length, and hence the excited state energies, of the carotenoid can be altered by protein binding site-induced structure changes to the molecule. This is particularly likely if the carotenoid has extended π-electron conjugation that may be either planarized with the linear chain or twisted in a way that decouples terminal π-bond(s) from the conjugation completely, resulting in changes in effective conjugation length. These effects produce diverse energy transfer pathways and efficiencies in light-harvesting proteins described in the following sections.

Purple Bacterial Antenna Complexes

The exemplary system for the transfer of energy between carotenoids and BChl-*a* is the LH2 antenna of purple bacteria (Figure 2A).[7] The structure of this complex revealed that the fundamental building block is an $\alpha\beta$-polypeptide subunit pair that binds two strongly coupled BChl-*a* molecules absorbing at ~850 nm (B850), one monomeric BChl-*a* molecule having an absorption band at 800 nm (B800), and one carotenoid molecule spanning the membrane in close contact with both the B800 and B850 molecules.

The carotenoid composition varies substantially among species of purple bacteria, but linear carotenoids with conjugation lengths (*N*) of 9−13 are predominant. All LH2 complexes studied so far exhibit ultrafast transfer of energy from the S_2 state as initially reported by Shreve et al.[8] Many studies have demonstrated that the S_2 state has a sub-100 fs lifetime in LH2, corresponding to the S_2-mediated energy transfer route in LH2 operating with an efficiency of 40−60% in LH2 complexes with carotenoids having an *N* of 9−12.[5,9,10] Using LH2 complexes lacking the B800 BChl-*a*, a branching ratio of ~2:3 for energy transfer to B800 and B850 BChl-*a* molecules was determined in LH2 of *Rps. acidophila*.[9] The experimentally measured energy transfer rates were successfully reproduced by calculations invoking the BChl-*a* excited state associated with the Q_x absorption band as the energy acceptor.[5,11]

An S_2-mediated energy transfer channel was also reported in the LH1 complex from purple bacteria, which is the inner antenna system surrounding the reaction center. In this complex, S_2-mediated energy transfer ranges from 60 to 70% for neurosporene ($N = 9$), decreases to ~50% for carotenoids with an *N* of 10−11, and further decreases to 40 and 30% for carotenoids with *N* values of 12 and 13, respectively.[12]

The origin of this dependence lies in the fact that the intrinsic S_2 lifetime becomes shorter with an increasing *N*.[13] Consequently, in longer carotenoids, S_2-mediated energy transfer must compete with shorter intrinsic S_2 lifetimes, resulting in less efficient energy transfer, even though the energy transfer rates remain nearly independent of *N*.[12] Alternative hypotheses invoking so-called "dark" states in energy transfer have also been suggested (Figure 1),[10] but the role of these states remains the subject of considerable debate. (For a recent review of this topic, see ref 4.) An interesting issue is that only minor changes in spectral overlap between the carotenoid S_2 emission and Q_x absorption are expected at room temperature due to the broad S_2 emission profile. However, recent experiments conducted at 10 K demonstrated a significant

decrease in S_2 energy transfer efficiency compared to the value at room temperature.[14] This decrease was proposed to be caused by a narrowing of the emission and absorption bands at low temperatures.

As suggested by Figure 3, transfer of energy from the S_1 state is also possible. However, even though the S_1 energies of most carotenoids are higher than energies of the S_1 states of BChl-*a*, the S_1-mediated energy transfer route drops off precipitously for carotenoids with N values of >10.[14−16] When neurosporene ($N = 9$) is present in LH2, the efficiency is 92−95%. It drops below 90% for spheroidene ($N = 10$) and is around 80% for spheroidenone which has the same number of C═C bonds as spheroidene, but with the conjugation extended to a carbonyl (C═O) group. The efficiency drops below 20% when $N = 11$. A very similar N dependence was found for LH1 reconstituted with different carotenoids.[12] Carotenoid-to-BChl energy transfer times involving the S_1 state were reported to vary between 1 and 2 ps,[14−16] which are ∼1 order of magnitude slower than those for the S_2 channel.

It is tempting to assign the absence of the S_1 channel in longer carotenoids to the B800 pigment being at an overly high energy to act as an energy acceptor, but this explanation does not hold because both B800 and B850 accept energy from the carotenoid S_1 state.[17] In addition, the decrease in the level of energy transfer from an N of 10 to an N of 11 was also observed for LH1 complexes which have no B800.[12] Moreover, the S_1 channel exhibits essentially no temperature dependence,[14] indicating that factors besides spectral overlap are involved. A possibility is that the sudden decrease in the level of energy transfer is caused by opening a new channel involving the carotenoid S^* state (Figure 1), which is able to transfer energy to BChl with only low efficiency, but it is also known to be a precursor of carotenoid triplet state formation.[18] Since the triplet yield increases with an increasing N,[19] the absence of significant S_1-mediated energy transfer for $N > 10$ forms may be attributed to population being funneled to the S^* state.

Another interesting proposal was offered by Ritz et al.,[20] who calculated carotenoid−BChl-*a* interaction energies and showed that the strength of this interaction depends on whether the methyl groups of the carotenoids are positioned asymmetrically or symmetrically with respect to the center of the π-electron conjugation in the molecule. Symmetrical positioning of methyl groups, which occurs in $N = 11$ carotenoids, is computed to weaken the interaction and lead to a decrease in energy transfer efficiency. Although this finding has never been experimentally rationalized, it remains an intriguing idea regarding how energy transfer in purple bacterial antenna may be controlled.

Antenna Systems of Green Plants

Green plants assemble a complicated network of Chl-*a*-containing antenna pigment−protein complexes. Energetic considerations (Figure 3) suggest that the S_1 pathway will be largely suppressed whereas transfer of energy from the S_2 state to the Q_x state of Chl-*a* will be favored. Indeed, the lack of energy transfer via the S_1 state of carotenoids has been confirmed experimentally, but its absence is, in some Chl-*a*-based antenna, compensated by a very efficient S_2 pathway. The most abundant antenna complex of this type is the LHCII protein (Figure 2B) which resides on the outermost periphery of the Photosystem II reaction center. Besides Chl-*a*, LHCII contains Chl-*b*, two luteins ($N = 10$), one neoxanthin ($N = 9$), and one violaxanthin ($N = 9$).[21] In this complex, the S_2 pathway of carotenoid-to-Chl energy transfer is utilized almost exclusively. The S_2 lifetimes of lutein and neoxanthin in LHCII are in the sub-100 fs range, resulting in efficiencies of 60−70%.[22−24] The key role of both lutein molecules in carotenoid-to-Chl energy transfer has been clearly established, and transfer of energy from the S_2 state of neoxanthin has been also demonstrated; however, its efficiency ranges from <10%[23] to >50%.[24] This uncertainty originates from the inability to selectively excite carotenoids in a manner independent of Chls in LHCII. Also, the question of whether Chl-*b* or Chl-*a* molecules are primary acceptors has been extensively debated.[22,24] Carotenoid absorption overlapping the Soret band of Chl-*b* complicates the analysis. Nevertheless, it is now clear that some fraction of acceptors are Chl-*b*, but the precise ratio of Chl-*a* and Chl-*b* acceptors remains an open question. A very similar pattern of carotenoid-to-Chl energy transfer was described in the peripheral Lhca4 complex of PSI from plants, which is similar to LHCII but contains only lutein and violaxanthin.[25] Studies of the PSI and PSII core antenna that contain only β-carotene have also revealed an active S_2 pathway.[26,27] Tuning the interaction between β-carotene and Chl-*a* can change the efficiency of the S_2 pathway significantly, as shown by efficiencies ranging from nearly 60% in the PSI core to 30% in the inner antennae of PSII.[26,27]

Transfer of energy from the carotenoid S_1 state is less favorable due to the high energy of the Chl acceptor states. The pathway from S_1 to Chl-*a* may be marginally active in complexes containing the shorter carotenoids, neoxanthin, violaxanthin, and lutein. Efficiencies reported for the transfer of energy from the S_1 state of these carotenoids did not exceed 15% in LHCII and CP29 complexes.[22,24] A slightly

higher efficiency of ~20%, caused likely by the presence of low-energy Chl-*a* molecules in this complex, was found in the Lhca4 peripheral antenna of plant PSI.[25] On the other hand, no evidence of the S_1-mediated channel was found in LHCII complexes reconstituted with $N = 9-11$ carotenoids.[28] Similarly, no energy transfer from the S_1 state was found in CP43 and CP47 complexes containing exclusively β-carotene.[26,27] In the PSI core that also contains only β-carotene but has low-energy Chl-*a* molecules, some activity of the S_1-mediated channel was reported,[27,29] but its efficiency did not exceed 20%. Interestingly, the inability to transfer energy from the S_1 state in some antenna complexes has been proposed to be compensated by an energy transfer channel using vibrationally hot S_1 as an energy donor. This pathway was suggested by two-photon excitation experiments which allow for direct excitation of the carotenoid into its S_1 state.[30] A subpicosecond increase in Chl-*a* emission after two-photon excitation of the S_1 state in the LHCII complex was reported and assigned to the transfer of energy between a vibrationally hot S_1 state of lutein and Chl-*a*.[30] The same channel was also reported in the PSI core where it likely accounts for ~20% of the total energy transfer.[29]

Although it seems that the role of the carotenoid S_1 state in light harvesting is only minor in plants and green algae, it may have a key function in regulating energy flow within antenna complexes. It has been proposed that the S_1 state of some carotenoids may be low enough to quench excited Chl-*a* via the transfer of energy to the carotenoid S_1 state.[31] Evidence of carotenoid S_1 state population after excitation of Chl-*a* has been reported in a transient absorption experiment,[32] supporting the notion that a reverse energy transfer channel is possible. Whether this pathway constitutes the long-sought mechanism of nonphotochemical quenching in higher plants remains an open question. Indeed, several alternatives have also been proposed.[33−35]

Antennae of Marine Algae

Another group of proteins utilizing carotenoids as light-harvesting pigments derives from marine algae that employ predominantly peridinin and fucoxanthin which contain a conjugated carbonyl group. This moiety causes the spectroscopic features and excited state dynamics of the carotenoid to be dependent on the polarity of the environment.[36,37] The dependence on polarity is caused by the electron-withdrawing nature of the conjugated carbonyl which leads to a stabilization of an intramolecular charge-transfer (ICT) state in polar environments.[36,37] The major effect of the ICT state is that it modulates the lifetime of the S_1 state with which it is electronically coupled. Besides the effect on the S_1 lifetime which becomes shorter in a polar environment, the S_2-S_1 energy gap decreases when a carbonyl group is introduced. The S_2 energy of carbonyl carotenoids is significantly lower than in their noncarbonyl counterparts, but the S_1 energy remains largely unaffected (Figure 3). Thus, the coupled S_1/ICT state is sufficiently high to keep favorable spectral overlap with the Q_y band of Chl-*a*, while the S_2 state is shifted to lower energies to allow efficient capturing of green light of vital importance for underwater organisms.[37]

An excellent system utilizing this light-harvesting strategy is the water-soluble peridinin-Chl-*a*-protein (PCP) from the dinoflagellate *A. carterae*.[38,39] Its structure (Figure 2C) has been refined recently to 1.5 Å.[40] As opposed to those of other light-harvesting systems, the pigment stoichiometry in PCP is dominated (4:1 carotenoid:Chl ratio) by the carotenoid peridinin. Peridinin absorbs light in the 450−550 nm region and transfers energy to Chl-*a* with an efficiency of ~90%.[41] The S_2 state in PCP provides a channel that accounts for 20−30% of the total energy transfer efficiency.[42] The dominant energy transfer channel is via the S_1/ICT state which is more than 80% efficient.[42,43] The lifetime of the S_1/ICT state of peridinin in PCP is 2.5 ps[42] which is shorter by a factor of ~5 than in polar solvents. Using these data, the efficiency of the S_1/ICT channel was determined from the total energy transfer efficiency measured by fluorescence excitation spectroscopy.[44] It was found that the S_1/ICT-mediated energy transfer rate constant in native PCP is $\sim(3\ \text{ps})^{-1}$, which is consistent with an intrinsic S_1/ICT lifetime of peridinin in the PCP complex of ~16 ps.[42]

A major advantage of working with the PCP complex is that it is amenable to site-directed mutagenesis and reconstitution with different pigments.[40,45] Reconstitution of PCP with various Chls alters the position of the Q_y band from 650 nm (Chl-*b*) to 790 nm (BChl-*a*), providing a systematic variation of spectral overlap.[46] Experiments with these reconstituted complexes confirmed the applicability of the Förster mechanism and also showed that when the Q_y band of Chl is close to the maximum of the peridinin S_1/ICT emission, the energy transfer efficiency is even better than in native PCP.[44,46]

Site-directed mutagenesis conducted on specific amino acid residues in the PCP demonstrated that it is a robust system in that the peridinin-to-Chl energy transfer efficiency was found to be insensitive to changes in the local protein environment of the pigments,[40] yet while energy transfer efficiency remained largely unaffected, the change of a single amino acid (Asn-89 to Leu-89) dramatically altered the absorption spectrum of the complex. The absorption band of the longest wavelength-absorbing peridinin was shifted by 24 nm to a shorter wavelength despite no change in the structure of the PCP.[40] This clearly demon-

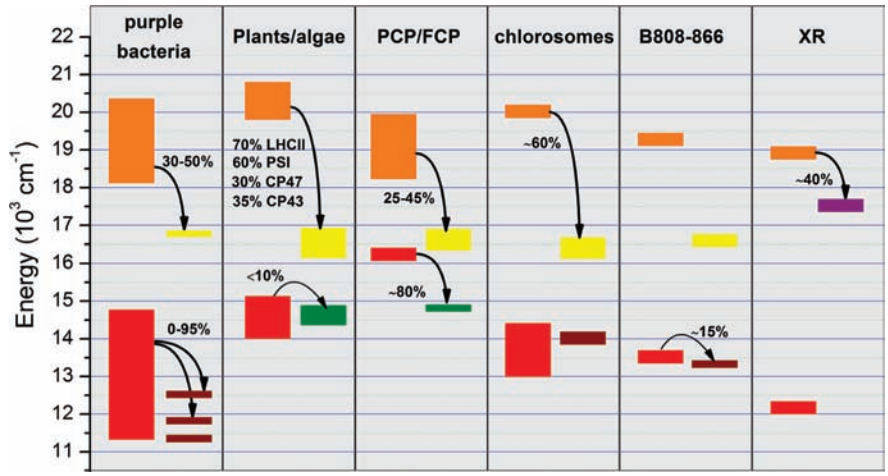

FIGURE 4. Summary of pathways and efficiencies of carotenoid-mediated energy transfer in light-harvesting systems from various sources. Energy is transferred either from the S_2 state of carotenoids (orange) to the Q_x bands of (B)Chl (yellow) or from the carotenoid S_1 state (red) to Q_y bands of BChl (brown) or Chl (green). The S_1 energy of the retinal chromophore in xanthorhodopsin is colored purple. The height of the rectangles corresponds to the variation in energy of the electronic states in complexes.

strates how the pigment environment can be engineered by nature to achieve broad absorption that expands light capture by the organism into the green spectral region.

The light-harvesting strategy of utilizing spectroscopic properties of carbonyl carotenoids also manifests itself in a membrane-bound antenna protein called LHC.[47] This protein is related to the Lhc family of plant protein complexes but binds Chl-*a*, Chl-*c*, and the carotenoids peridinin and diadinoxanthin. In this complex, peridinin transfers energy to Chl-*a* primarily via the S_1/ICT state, and the energy transfer rate is essentially identical to that in PCP.[47] Very similar behavior was reported in a related protein from the diatom *Cyclotella meneghiniana* that binds fucoxanthin instead of peridinin.[48]

Other Systems

Besides the three examples of antenna proteins described above, carotenoids have also shown their light-harvesting capability in the large BChl-*c*−*e*-containing antenna of green sulfur bacteria known as chlorosomes. These contain predominantly the carotenoids chlorobactene and isorenieratene possessing aryl terminal rings. Most likely due to tight packing of pigments within the chlorosomes, isorenieratene exhibits efficient energy transfer from the S_2 state. Efficiencies of >60% in *Chlorobium phaeobacteroides* have been reported.[49] No evidence of S_1-mediated energy transfer has been found, perhaps due to the fact that spectral overlap between the S_1 emission of isorenieratene, which has spectroscopic properties nearly identical to those of its nonphenolic counterpart β-carotene,[50] and the Q_y absorption of BChl-*e* is small.

A completely different energy transfer scheme was reported for the B808−866 antenna complex of the green bacterium *Chloroflexus aurantiacus*. This antenna system, which contains BChl-*a* and γ-carotene, is similar to the LH2 and LH1 complexes of purple bacteria, but unlike these antennae, the efficiency of carotenoid-to-BChl energy transfer is only 15%. The energy transfer pathway occurs from the S_1 state of γ-carotene.[51] Interestingly, no S_2-mediated pathway was observed, making the B808−866 complex the only known antenna that employs exclusively the S_1 pathway.

Light harvesting by carotenoids was also described in a novel system that does not contain (B)Chl. This is the so-called xanthorhodopsin from *S. ruber* which belongs to the large group of retinal-based energy transducers.[52] A few of these proteins from archea exhibited association with carotenoids, but only in xanthorhodopsin (Figure 2D) which binds the carotenoid salinixanthin has the carotenoid been shown to be able to transfer energy to retinal.[52] Because of the high energy of the acceptor state (~17200 cm^{-1}), only the S_2 channel is active, and it has an efficiency of 40%.[53]

Synthetic Antennae

The versatility and robustness of carotenoids in naturally occurring light-harvesting systems, summarized in Figure 4, have not gone unnoticed in attempts to design and synthesize nanoscale systems seeking to mimic and perhaps even improve upon the efficiency of the natural systems in light capture and solar energy conversion. A series of carotenoid−pyropheophorbide dyads having either zeaxanthin or fucoxanthin as the energy donor were reported to reproduce qualitatively the energy transfer efficiency observed in the natural systems.[54] For zeaxanthin, only the S_2 pathway was

active, and efficiencies of up to 15% did not come close to matching those of natural systems. With fucoxanthin as an energy donor, which has a higher S_1 energy than zeaxanthin, pyropheophorbide became accessible via the S_1 channel. The resulting efficiencies were 15−45%, depending on the orientation of the donor and acceptor. Pyropheophorbide as an energy acceptor was used again in a subsequent study employing peridinin and fucoxanthin as energy donors.[55] In this work, solvents with different polarities were used and revealed the potential for tuning the energy transfer efficiency of these carotenoids in artificial systems by changing the solvent polarity. Peridinin was found to transfer energy from its S_1/ICT state with 80% efficiency in benzene, which is nearly its efficiency in natural PCP. The efficiency decreased with increasing solvent polarity and became as low as 20% in the polar solvent, acetonitrile. The same trend was observed for fucoxanthin, but its efficiency was tunable over a narrower range between 13 and 23%.[55]

A synthetic $N = 11$ carotenoid covalently bound to purpurin in a dyad system provided an S_2 channel with an efficiency greater than 70%, thus exceeding that in a natural system.[56] Another version of the dyad employed two shorter ($N = 10$) carotenoids attached axially to the central Si atom of the Si-phthalocyanine. In this arrangement, the efficiency of the S_2 channel dropped below 70%, but the S_1 channel operated with nearly 90% efficiency, making this system competitive with the most efficient carotenoid-based antenna found in nature.[57] Moreover, the properties of this carotenoid−phthalocyanine dyad can be tuned by solvent polarity as evidenced by the fact that in nonpolar solvents energy transfer occurs whereas in polar solvents electron transfer takes place.

Switching between energy and electron transfer was also achieved in a series of carotenoid−phthalocyanine dyads, in which a single $N = 9$, 10, or 11 carotenoid was attached to the tetrapyrrole macrocycle.[58] For the shortest carotenoid, both the S_2 and S_1 states were active in energy transfer, with efficiencies of 70 and 20%, respectively, whereas for $N = 10$ and 11 carotenoids, only the S_2 pathway remained active and the efficiency dropped to 60 and 24%, respectively. To a certain extent, this is reminiscent of the N dependence of energy transfer observed in purple bacterial antennae, but in these cases, the S_1 pathway is inhibited for even shorter π-electron-conjugated molecules because of the high S_1 energy of the acceptor. Remarkably, these dyads were capable of mimicking the critical photoprotective function of higher plants evidenced by the two longer carotenoids quenching the excited S_1 state of phthalocyanine.[59] Thus, these systems hold great promise for the design and construction of novel synthetic solar energy conversion devices that not only carry out light harvesting as described in this Account but also dissipate excess absorbed energy not required for the specific photochemical process at hand.

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FOOTNOTES

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