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Molecular Topography and Energy Transfer in Solar Energy Harvesting Pigment Proteins†

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태양에너지를 채취하는 색소단백질들의 분자 토포그라피와 에너지전달현상

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요 약

디노프라젤레이트(dinoflagellate)들의 광채취색소단백질들은 안테나색소복합체들 내에서 카로테노이드(페리디닌)로부터 크로필 *a*로 실질적으로 100%의 효율을 갖는 에너지전달현상을 보여준다. 이와같이 디노프라젤레이트에서 광합성을 위한 태양에너지의 채취가(특히 靑색광에서) 높은 효율로 일어나는 것은 단백질표면의 갈라진 틈안에 위치한 페리디닌과 프로로필 *a*의 독특한 분자배치에 기인하는 것이다. 고등식물에서 가로테노이드와 크로로필 *a* 사이에 일어나는 에너지 전달메카니즘에 관해서도 디노프라젤레이트 안테나색소복합체들과 비교해서 고찰하였다. Algae에서 광합성을 위한 태양에너지, 특히 赤색광의 채취를 다룬 하나의 예로서 *Chroomonas* species의 보조광합성색소단백질인 크로오오모나스 피코시아닌의 분자토포그라피와 에너지전달도 역시 고찰하였다.

Introduction

The reaction center chlorophyll *a* (chl *a*) in plants serves as the primary photoreceptor for photosynthesis. The reaction center chl can be directly excited by red light. However, the major excitation of the photosynthetic reaction center apparatus is through the antenna pigments that largely cover the visible spectrum of solar radiation. The light absorption by the reaction center chl is considerably lower than that of the antenna pigments and the absorption spectrum of chl does not adequately span the solar spectrum, particularly in the region of blue, yellow and part of red. The antenna pigments include carotenoids and phycobilins, as well as chl *a*, *b* and *c*.

In this paper, we will review the mechanisms by which energy absorbed by various antenna or light harvesting pigment proteins is transfered to chl. The latter can be either another antenna chl, or the reaction center pigment. The mechanism of energy transfer from the antenna chl to the reaction center chl will not be discussed in this review.

Two specific systems of the energy transfer from antenna pigments to chl will be discussed. These include(1) the molecular topography

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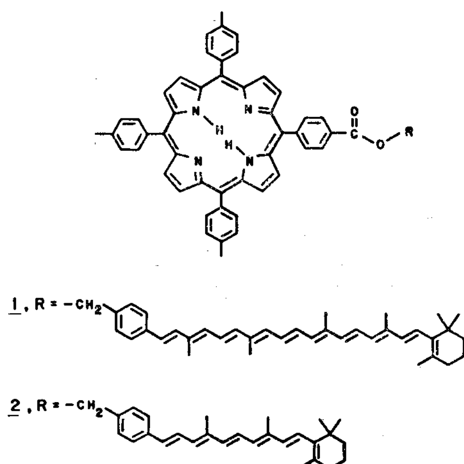

Scheme 1. Chemical structure of caroteno-*meso*-tetraarylporphyrins. Compound 3 (structure not shown) is equivalent to the *ortho*-substituted analog of compound 1, which carries the polyene substitute at *para* position (1).

of light-harvesting pigment proteins and the energy transfer from carotenoids to chl in dinoflagellates and (2) the molecular topography of phycocyanin in *Chroomonas* and its role in energy transfer to chl.

This review is intended to be neither comprehensive nor exhaustive. Because of the limited space, the review will be confined to the work from this laboratory, with selected references from other laboratories which are immediately pertinent to the present discussion.

The molecular topography and energy transfer in dinoflagellates

1. The energy transfer from carotenoid to chlorophyll

Dinoflagellates such as *Glenodinium* sp., *Amphidinium carterae*, *A. rhyncocephaleum*, *Gonyaulax polyedra*, *G. tamarensis* and *Cachonina niei* contain water soluble antenna pigment proteins consisting of four peridinin and one chl *a* molecules per protein of mol. wt. 30,000~35,000 (Siegelman *et al.*, 1977). The pigment molecules are accommodated within a deep crevice of the protein which provides sufficient surface area on the crevice wall for the pigment binding (Koka and Song, 1977). Hereafter, these pigment proteins will be abbreviated simply as PCP.

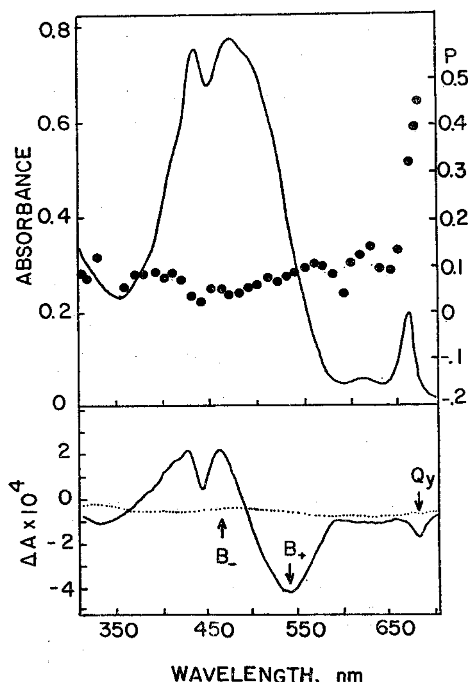

Fig. 1. Top panel: The absorption spectrum of PCP isolated from *G. polyedra* in 2 mM tris-glcerol (1 : 4, v/v), pH 7.4, at room temperature. The fluorescence excitation polarization (solid circle) was recorded with respect to the chl *a* fluorescence at 675 nm and 200 K, by setting bandpass of 2 and 0.5 nm for emission and excitation, respectively.
Lower panel: The CD spectrum of PCP (*G. polyedra*) in 2 mM tris-glycerol (1 : 4 v/v) at room temperature. The base line for the CD cell and solvent is also indicated (dotted line). Three major bands of PCP are designated by arrows, as described in the text.

Fig. 1 shows spectral characteristics (absorption, polarized fluorescence excitation, and CD) of PCP. Peridinin absorbs blue light, thus harvesting the light of 440~550 nm from the sunlight, which is not significantly absorbed by chl. Peridinin effectively transfers its absorbed energy to chl *a* (Song *et al.*, 1976b;

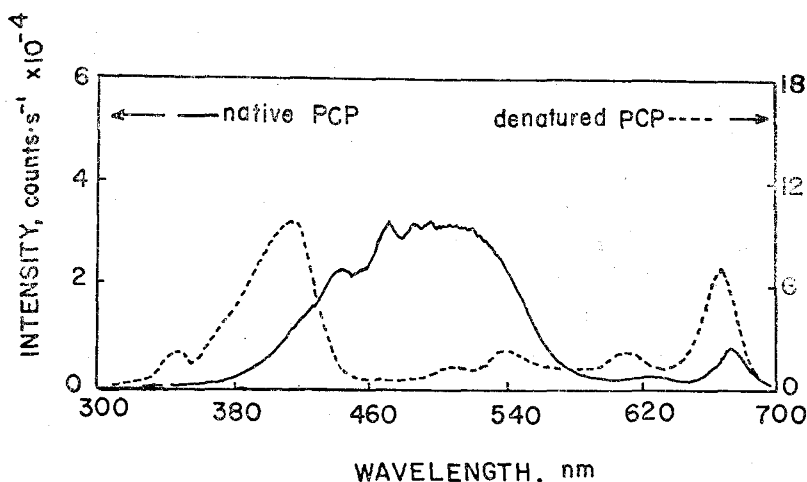

Fig. 2. The fluorescence excitation spectra of the native (solid line) and SDS-denature PCP (broken line) from *Glenodinium* sp. in trisglycerol (1 : 4, v/v) buffer at room temperature. The excitation bandpass was 0.4 nm, used for the single-photon counting spectrofluorometer. Note that the intensity scale for the denatured PCP is on the right ordinate.

Koka and Song, 1977). The energy transfer within PCP is measurable by monitoring the chl *a* fluorescence with excitation at 450~550 nm, where peridinin predominantly absorbs.

Fig. 2 shows the fluorescence excitation spectrum of PCP. The ratio of absorbance at the Q_y band (670~673 nm) of chl *a* to that at the blue absorption maximum (478 nm) of peridinin is 4, and is essentially identical to the ratio of excitation intensities at the chl Q_y and peridinin bands. This indicates that the energy transfer from peridinin to chl *a* is virtually 100 %. The efficient energy transfer in PCP is completely abolished by the denaturation of the protein (Song *et al.*,1976 b), suggesting that the structural integrity of PCP is required for the energy transfer. This point will be elaborated further in the next section.

2. The mechanism of energy transfer in PCP

The excitation of carotenoids in mixed solutions containing carotenoids and chl *a* does not result in significant energy transfer to the latter even at low temperatures (Song and Moore, 1974; Moore, 1975). Similarly, we have not been able to demonstrate the energy transfer from peridinin to chl *a* in solution. Recently, Moore *et al.* (1980) have synthesized an analog of the carotenoid-chl complex by covalently linking a polyene to the aryl porphyrin. No significant energy transfer from the former to the latter was observed (*vide infra*). Thus, the lack of energy transfer in solution offers a clue to the structural integrity of PCP necessary for maximum energy transfer. Apparently, the energy transfer does not occur in solution, mainly due to the fact that the carotenoid fluorescence has a quantum yield less than 10^{-6}, and the fluorescence is too short lived (Song and Moore, 1974).

We now examine the structural integrity of PCP spectroscopically. First, the absorption spectrum of the native PCP reveals a shoulder at 525 nm (Fig. 1), which is more prominently resolvable at low temperature. The CD spectrum of the native PCP exhibits a strong negative ellipticity in this region (extremum at 545 nm). A strong, positive ellipticity is also seen with extremum at 462 nm. Both CD extrema occur within the main absorption band ($^1B \leftarrow A$ transition) of peridinin, indicating that the CD splitting arises from two excited states as the result of electronic interactions among peridinin mole-

cules. The most likely interaction which accounts for the split CD spectrum is exciton (or resonance) interaction between two peridinin molecules (dimer) (Song *et el.*, 1976b; Koka and Song, 1977; Song, 1978). Since there are four peridinin in PCP, two sets of the dimeric molecule pair are involved in the exciton interaction. These two sets of the dimer seem to be situated sufficiently far apart from each other, since exciton interactions involving all four peridinin molecules would have resulted in more complex, four-extrema CD spectrum (Kasha, 1965).

As has been emphasized earlier, it is important to deduce the molecular topography of four peridinin and one chlorophyll *a* molecule in PCP, as the molecular integrity of the light harvesting pigement protein is essential for the efficient energy transfer from peridinin to chl *a*. Since excitation of the exciton states (designated as B_+ and B_- for the negative and positive CD components of the peridinin absorption band) leads to the fluorescence of chl *a* in PCP (Fig. 2), orientations of their transition dipoles can be detemined by the fluorescence excitation polarization relative to the orientation of the chl *a* Q_y emission moment. Fig. 1 includes a typical set of the polarization data, yielding polarization degrees of 0.05-0.1 for the B_+ and B_- bands of peridinin, respectively. This result suggests that the B_+ and B_- transition dipoles are both oriented approximately 45° with rerpect to the Q_y transition dipole of chl *a* (Song *et al.*, 1976b). The fact that the polarization of both exciton bands is constant and that their relative absorption intensities are of about equally allowed tarnsition (Fig. 1), neither linear (→→) nor completely stacked (⇆) peridinin dimer is consistent with the observed data. Therefore, the most likely molecular topography is that shown in Fig. 3, in which the B_+ and B_- transition dipoles are oriented about 45° relative to the Qy transition dipole of chl *a*.

We now turn to the implication of the molecular topography of PCP as deduced from spectroscopic data. In our previous analysis (Song and Moore, 1974), it was concluded that carotenoids were not suited as a primary

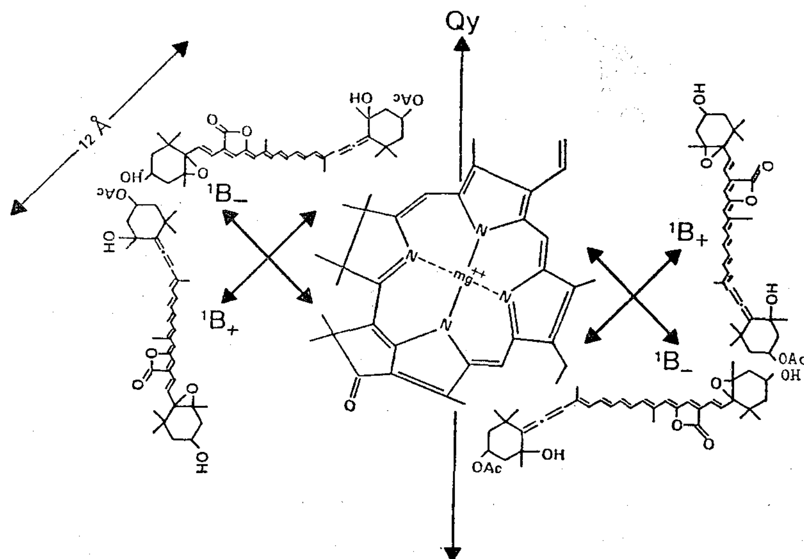

Fig. 3. The molecular topography of PCP from marine dinoflagellates. Two molecules form excition pairs, resulting in two exciton states, B_+ and B_-, corresponding to the CD extrema shown in Fig. 1. The Q_y transition dipole axis of chl *a* is also shown.

photoreceptor. Among several reasons, an extremely short lifetime due to subpicosecond internal conversion from the lowest singlet excited state was cited as the most critical barrier for carotenoid or carotenoprotein to overcome as a primary photoreceptor (*vide infra*). Carotenoids referred to here exclude retinylic polyenes such as those in rhodopsin and bacteriorhodopsin.

The problem of short lifetime of the excited state in carotenoids as a secondary photoreceptor (antenna) can be partly overcome by interactions between the excited states of more than one carotenoid molecules and between those of carotenoid and acceptor molecules (chl *a* in the case of PCP).

The dimeric exciton interaction shown in Fig. 3 can lead to the lengthening of lifetime of the peridinin excited state, thus enhancing the probability of energy transfer from peridinin to chl *a*. This is illustrated in Fig. 4.

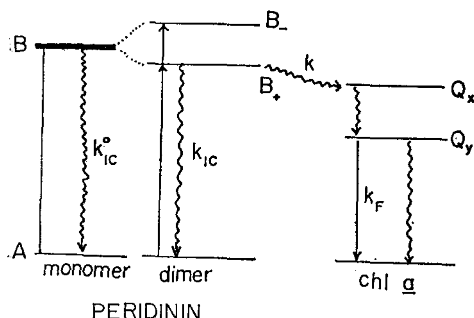

Fig. 4. The energy level diagram for PCP. It is assumed that the rate constant for internal conversion, k°_{IC}, in monomer is substantially greater than k_{IC}, for dimer. The rate constant for energy transfer from the lower exciton state, B_{+}, to chl *a* is $k \geq 1 \times 10^{11}$ sec^{-1}.

In addition, the excition coupling of the B excited state of two peridinin molecules in the dimeric array brings the B_{+} state closer to the energy accepting Q_x and/or Q_y states of chl *a*, which should facilitate the energy transfer. It is further possible that the excited states of peridinin and chl *a* are coupled (e.g., via near degenerate exciton interactions). The extent of such a coupling

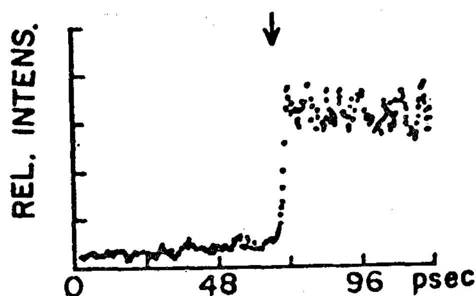

Fig. 5. The chl *a* fluorescence rise in PCP in 2 mM tris buffer by psec pulse excitation (arrow) of the lower dimeric exciton band, B_{+}, (Figs. 1 and 4) of peridinin at 527 nm.

cannot be ascertained for PCP until mutual spectral perturbations of peridinin and chl *a* are fully resolved.

Fig. 5 shows the picosecond streak camera tracing of the fluorescence rise and decay of chl *a* in the PCP complex by exciting the peridinin absorption band at 527 nm. From the rise of the fluorescence of chl *a*, the energy transfer rate constant was estimated to be $k_{et} \simeq 10^{11}$sec^{-1}, with the fluorescence rise-time of about 10 psec (Song *et al.*, 1980). More recent picosecond measurements enabled us to resolve a rise-time of 8 psec (unpublished data).

Although the dimeric exciton array of peridinin in PCP appears to be requisite for the maximum energy transfer efficiency, it is not certain how wide spread such interactions are among the light harvesting carotenoproteins in nature. Of course, it is possible to transfer the excitation energy from carotenoid to chl via other mechanisms without involving dipole-dipole coupling (exciton) for carotenoid molecules. One such mechanism involves sufficient electronic interactions between the donor excited state of carotenoid and the acceptor excited state of chl, as mentioned previously. The dipole-dipole coupling and/or electron exchange between the donor and acceptor molecules, as well as charge transfer between them, could contribute to the electronic interactions.

Goepheer (1972) suggested that for effective energy transfer from the non-fluorescent carotenoid to chl *a* a close spatial relation between the donor and acceptor molecules should occur. Consistent with this view, Razi Naqvi (1980) suggested that the energy transfer from the non-fluorescent carotenoid to chl *a* occurred by the exchange mechanism (Dexter, 1953), rather than by the Förster's long-range transfer based on ***very weak*** dipole-dipole coupling (Förster, 1959), since carotenoids hardly fluorescence ($\phi_F \sim 0$). *

The efficiency of energy transfer via the Förster mechanism is given by the following equation:

$$\phi_{et}=\left[1+\frac{1}{8.8\times10^{-25}\eta^{-4}\kappa^2\phi_F J}\left(\frac{1}{R^6}\right)\right]^{-1}$$

where η is the refractive index, κ is the orientation factor, R is the distance between donor and acceptor dipoles, and J is the spectral overlap integral between the donor fluorescence and acceptor absorption bands. From this equation, it can be seen that the energy transfer efficiency is directly related to the donor fluorescence quantum yield, ϕ_F. This reasoning has previously been expressed in discussing the lack of energy transfer in the mixed solution of β-carotene and chl *a* (Song and Moore, 1974).

For PCP, the Förster's mechanism of energy transfer was ruled out on somewhat different grounds (Song *et al.*, 1976). Thrash *et al.* (1979) argued that the Förster's mechanism accounted for the efficient energy transfer from carotenoid to chl by assuming that the low-lying ^{1}Ag state of polyenes was the energy-donating state of carotenoids. Razi Naqvi (1980) does not support this proposal, as mentioned above.

Dirks *et al.* (1980) synthesized carotenoids covalently linked to *moso*-tetraarylporphyrin (1 and 2) as models for antenna pigment complexes composed of carotenoid and chl in 1 : 1 ratio. These synthetic models are also useful for ascertaining the spatial relationship or molecular topography of light-harvesting pigment complexes. No energy transfer from the carotenoid moiety to the porphyrin was observed in 1, while the energy transfer in 2 was found to be about 80%. This is not surprising since the polyene of 2 is fluorescent ($\phi_F \sim 10^{-3}$) and the Förster critical distance at which the transfer is 50% efficient is 13 Å, while the carotenoid moiety of 1 has $\phi_F < 10^{-6}$.[6] However, when the carotenoid in 1 was linked so that the chain substitution is at the ***ortho*** position of the phenyl ring (3), forcing the former to fold over the porphyrin ring, a significant fraction of the excitation energy absorbed by the carotenoid moiety was transfered to the porphyrin (Dirks *et al.*, 1980). The energy transfer observed with 3 (*ortho* 1) is apparently due to the stacking of the carotenoid chain over the porphyrin. Does the exchange mechanism, then, fully account for the energy transfer from the non-fluorescent donor (carotenoids) to chl? This question is examined below.

The energy transfer from the triplet state (^3Q_y) of chl to the triplet state (^{3}B) of β-carotene occurs efficiently both ***in vivo*** and ***in vitro*** (Chessin *et al.*, 1966; Mathis, 1969; Witt, 1971). This observation was used in concluding that the energy transfer from the singlet excited state (^{1}B) of β-carotene to chl occurs via the electron exchange mechanism (Razi Naqvi, 1980), as in the triplet-triplet energy transfer which proceeds via electron exchange.

The energy transfer rate constant via electron exchange can be written as follows (Ermolaev, 1967):

$$k_{ex}=k_0e^{-R}$$

where k_0 ($=10^{13}\text{sec}^{-1}$) is the maximum value

*It is worthwhile to investigate if the peridinin dimers in PCP can be made fluorescent by selectively removing chl *a* from the PCP protein without desrupting the structural integrity of the protein and peridinin. So far, our attempts to remove chl *a* selectively have not been successful.

corresponding to collision frequency at an infinitesimal separation between donor and acceptor molecules ($R \rightarrow 0$Å) and the "effective" acceptor concentration of $\sim$5M if both donor and acceptor molecules are fixed as in PCP and compound 3. If we assume that separation (R) between the carotenoid and porphyrin moieties in 3 is$\sim$5Å, a reasonable value, corresponding to the "effective" concentration greater than 1M, the rate constant for the exchange transfer is predicted to be $5 \times 10^{8} sec^{-1}$, from the above equation. This value is too low to account for the 100% efficiency of energy transfer and the rise time of $<$10 psec for the chl *a* fluorescence in PCP (Fig. 5). *At* $R=3$Å, $k_{ex} \simeq 5 \times 10^{11}$ sec^{-1} is calculated. At this separation, the energy transfer starts to compete with the radiation less decay in carotenoids. The radiative lifetime of carotenoids (e.g., β-carotene and lycopene) is 1 nsec (Song and Moore, 1974). The mean lifetime is less than 10 psec and 1 psec, assuming $\phi_F \leq 10^{-5}$and$\leq 10^{-6}$, respectively. The latter ϕ_F is more reasonable, since an upper limit of $\phi_F < 10^{-6}$ can be deduced from the fact that no fluorescence is detected in reasonance Raman measurements of carotenoids (M.A.J. Rogers, cited in Dirks *et al.*, 1980). If we allow a factor of 100 for anomalousyl long radiative lifetimes in polyenes due either to torsional deactivation of the ^{1}B excited state (Song *et al.*, 1976a) or the forbidden $^{1}A_g$ state as the lowest excited state (Hudson and Kohler, 1974), which remains unresolved for carotenoids (Song, 1977). the radiative lifetime will be on the order of 100 psec, and the mean lifetime will be 0.1psec. Thus, the exchange rate of 5×10^{11} sec^{-1} starts to compete with the radiationless decay rate in carotenoids, but would not fully account for high efficiencies of the energy transfer from carotenoids to chl *in vivo* or in PCP. However, in the PCP system, the relative contribution of exchange transfer cannot be asceratined since the degree of increase in the lifetime (B_+) of peridinin caused by the dimeric exciton interaction is not known.

At the separation distance of 3Å between donor and acceptor molecules, energy donor and acceptor molecules can no longer be treated as separate molecules, and the pair should really be viewed as one "super molecule." Electronic interactions such as charge transfer and exciton resonance between the two molecule cannot be neglected for the "super molecule," as the absorption spectrum of the pair will no longer be a simple composite of the spectra of each molecule.

In summary, we propose that the mechanism responsible for the maximum efficiency of energy transfer from peridinin to chl *a* in PCP involves both electron exchange and exciton interactions between peridinin and chl *a*, which are facilitated by the near-degeneracy of the B_+ state of peridinin with the Q_x state of chl *a* (cf., Fig. 4) and by the lengthening of lifetime of singlet excited state (B_+) for peridinin.

The molecular topography and energy transfer in phy cocyanin

We now describe another light harvesting pigment protein, phycocyanin from *Chroomonas* species of crytomonad algae. The phycocyanin consists of four subunits of the form $\alpha\alpha'\beta_2$. The two small subunits, α and α', cannot be differentiated by their molecular weights as determined by conventional methods such as SDS gel electrophoresis and gel permeation chromatography; the larger β subunit contains two chromophore molecules, one of which is phycocyanobilin.

A dipole-dipole exciton coupling model was applied to interpret spectral properties of *Chroomonas* phycocyanin (Jung *et al*,1980). Two main CD extrema, one with a strong negative band and the other with a positive band, are probably due to the result of exciton coupling of two phycocyanobilin

molecules contained in the two β-subunit polypeptides. The visible absorption spectrum of *Chroomonas* phycocyanin with two main peaks at 645 and 583nm were analyzed to yield five spectral components with their maxima at 573, 592, 617, 636, and 652nm. The 592 and 652 bands are the split bands of phycocyanobilins in the β-subunit, the 617nm band assigned to phycocyanobilin in the α subunit, and the 636nm band assigned to the chromophore in the α′ subunit (Fig. 6; Jung *et al.*, 1980). The C′ chromophore in the β-subunit (Fig. 6) is probably a phycobilibiolin

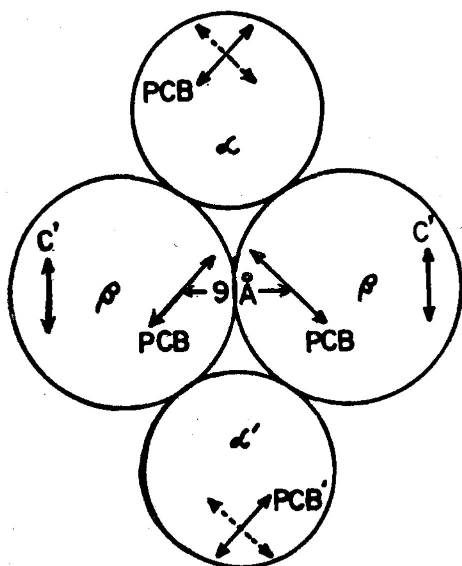

Fig. 6. A possible chromophore topogrophy for the *Chroomonas* phycocyanin, with four protein subunits, $\alpha\alpha'\beta_2$. Chromophores PCB and *C′* are phycocyanobilin and phycoerythrocyanin or phycoerythrocyanin-like bilin, respectively.

type found in the α-subunit of the cyanobacteral phycoerythrocyanin (Bryant *et al.*, 1976).

Based on the proposed excition coupling model (from CD) and the fluorescence excitation polarization spectrum, a tentative molecular topography of *Chroomonas* phycocyanin is described in terms of spectroscopic parameters, including the inter-chromophore distance of the exciton interacting phycocyanobilins (from CD) and the relative orientations of every chromophore molecule existing in the biliprotein (from fluorescence polarization) (Fig. 6).

To account for the five-component composite absorption spectrum of the *Chroomonas* phycocyanin, we note that the CD spectrum shows +(592nm) and−(657nm) extrema, which can be attributed to a dipole-dipole coupling (exciton) between the two interacting chromophore molecules of the β-subunits (Fig. 7).

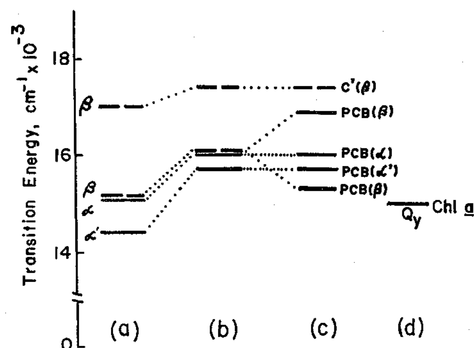

Fig. 7. The energy level diagram (transition energy in cm^{-1}) illustrating the effect of exciton interactions between two β-subunit chromophores of phycocyanin from *Chroomonas* species.
(a) The energy levels of chromophore in the subunits of phycocyanin in 9M urea-HCl.
(b) The hypothetical energy levels of chromophores in the absence of the dipole-dipole coupling between the β-subunit chromophores.
(c) The energy levels of chromophores after the dipole-dipole coupling(exciton) between the β-subunit chromophores.
(d) The Q_y state of chl *a*.

The α and α′ subunit proteins tend to strengthen the dipole-dipole coupling as the result of a favorable orientation of the two chromophore transition dipoles on the two β-subunits (Jung *et al.*, 1980). The net result is an enhanced resolution of the two exciton bands in the low temperature fluorescence excitation spectrum and an enhanced fluorescence from

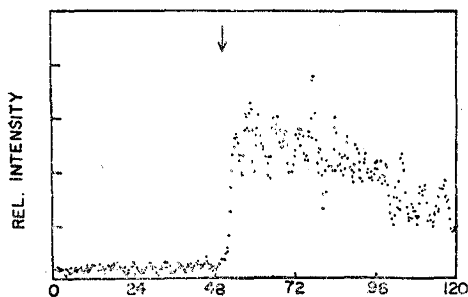

Fig. 8. The fluorescence rise and decay of *Chroomonas* phycocyanin in 10 mM phosphate boffer, pH 6, at room temperature. Psec excitation pulse (arrow) at 527 nm. Emission wavelength 680 nm.

the lower exciton state of the phycocyanin (Jung *et al.*, 1980).

Fig. 8 shows the picosecond streak camera tracing of the fluorescence rise and decay of the *Chroomonas* phycocyanin by exciting at the second harmonic of the neodymium: glass mode-locked laser (527 nm) which is preferentially absorbed by the second chromophore (C' in Fig. 7) on β-subunit. It should be recalled that there are two chromophores on each β-subunit; one is involved in the dipole-dipole coupling with another β-subunit, while the second chromophore is not directly coupled to its counterpart (Jung *et al.*, 1980). The fluorescence rise (monitored as fluorescence emission from the lower exciton state, cf. Fig. 7) approximately follows the time resolution of the streak camera itself, suggesting that the interchromophore energy transfer time is less than 10 psec. This result is in agreement with the energy transfer time constant of less than 8 ps (Kobayashi *et al.*, 1979). The fluorescence decay curve (Fig. 8) yields the fluorescence lifetime of 1.35 nsec; this value is comparable with the values of 1.55 nsec and 1.42 nsec from 30 phase-shift and modulation measurements at MHz, respectively (Jung *et al.*, 1980). Clearly, the relatively long fluorescence lifetime of phycocyanin reveals an interesting contrast with that of phytochrome which has a similar chromophore but exhibits subnanosecond lifetime due to an efficient primary photoprocess in the excited state (Song *et al.*, 1979).

The fast energy transfer from one chromophore to another with in each β-subunit can be explained in terms of a favorable spectral overlap between the fluorescence spectrum of the donor chromophore and the acceptor (exciton state) absorption spectrum (Jung *et al.*, 1980). Spectral overlap is also favorable for the energy transfer via the α subunit, the latter then transferring energy to the lower exciton state of the βsubunit.

In order to resolve various energy transfer pathways, it is necessary to measure energy transfer within the phycocyanin subunit assembly at different wavelengths for excitation and at faster time scale. Porter *et al.* (1978) and Searle *et al.* (1978) were able to resolve the fluorescence risetimes of B-phycoerythrin (0 psec), R-phycocyanin(12 psec) and allophy cocyanin(22 psec) in *Porphyridium cruentum*, demonstrating the order of energy tanrsfer sequence. Using psec absorption spectroscopy, Kobayashi *et al.* (1979) have obtained the time constants for inter-subunit energy transfer of ~85 psec (monomer=$\alpha\beta$), ~56 psec (trimer=$\alpha_3\beta_3$) and ~32 psec (hexamer=$\alpha_6\beta_6$) for C-phycocyanin from *Phormidium luridum*. From these time constants, inter-subunit distances of R=39−42 Å, 44−48 Å and 36−39 Å were estimated, respectively. Thus, the Förster dipole-dipole mechanism seems to adequately account for the long range energy transfer within the phycocyanin subunits.

Since the lowest excited state of the *Chroo monas* phycocyanin is fluorescent, the energy transfer from phycocyanin to chl can take place with the Förster mechanism. However, the main advantage of having the lower exciton state in the *Chroomonas* phycocyanin is to enhance the energy transfer efficiency by increasing the spectral overlap between the phycocyanin fluorescence and chl *a* adsor

ption bands. The near-degeneracy of the fluorescent state of the phycocyanin with the Q_y band of chl *a* (cf., Fig. 7) will also facilitate tbe energy transfer via the exchange mechanism. However, the close proximity of the antenna phycobiliproteins and the chl *a* is not an absolute requisite for efficient energy transfer, in contrast to the carotenoid-chl systems discussed earlier.

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Abstract

The light harvesting pigment proteins of dinoflagellates exhibit essentially 100% efficient energy transfer from carotenoid (peridinin) to chlorophyll *a* within the antenna pigment complexes. The high efficiency of solar energy harvesing(particularly blue light) for photosynthesis in dinoflagellates is attributable to the unique molecular topography of peridinin and chlorophyll *a* within the protein crevice. The mechanisms of energy transfer from carotenoids to chlorophyll in higher plants have also been discussed in comparison with the dinoflagellate antenna pigment complexes. As an example of solar energy harvesting, particularly red light, for photosynthesis in algae, the molecular topography and energy transfer in the photosynthetic accessory pigment protein, *Chroomonas* phycocyanin, have also been discussed.

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