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Lateral energy transfer model for adjacent light-harvesting antennae rods of C-phycocyanins

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Abstract

Modeling of excitation transfer pathways have been carried out for the structure of *Spirulina platensis* C-phycocyanin. Calculations by Förster mechanism using the crystal structure coordinates determined in our laboratory indicate ultra-fast lateral energy transfer rates between pairs of chromophores attached to two adjacent hexamer disks. The pairwise transfer times of the order of a few pico-seconds correspond to resonance transitions between peripheral β155 chromophores. A quantitative lateral energy transfer model for C-phycocyanin light-harvesting antenna rods that is suggestive to its native structural organization emerges from this study.

Keywords: Light-harvesting; Photosynthesis; Phycobilisomes; Phycocyanobilin

1. Introduction

Photosynthesis is initiated by efficient absorption and transmission of solar light energy by light-harvesting antennae rods [1,2]. Studies on light-harvesting antennae proteins have resulted in providing an understanding of this highly efficient energetic phenomena [3,4]. A collective approach involving application of information gained from crystal structure analyses and a variety of spectroscopic studies into a theoretical framework along with the construction of useful models have enhanced our understanding of these natural bio-energetic systems [5]. The models studied include light-harvesting systems from purple bacteria, cyanobacteria, and green plants [6–8]. These studies have assumed additional significance in view of recent attempts to fabricate biomimetic, artificial nano-scale photodevices [9].

C-phycocyanin (CPC) belongs to one of the principal classes of light-harvesting antennae rod proteins in cyanobacteria. Crystal structures of CPCs determined, to date, have revealed that the general architecture of macromolecular assemblages are remarkably conserved across various species [10–17]. They consist of α- and β-subunit polypeptides, which exhibit high affinity for one another and associate into (αβ)-monomers. These monomers assemble into a $(\alpha\beta)_3$-trimer and two trimers constitute a $(\alpha\beta)_6$-hexamer disk. The cylindrical CPC disks are the basic functional blocks that stack one above the other forming the light-harvesting antennae rods. CPC with other similar antennae proteins such as Phycoerythrin (PE), Allophycocyanin (APC) along with linker polypeptides self-assemble into supramolecular light-harvesting complexes called phycobilisomes [7,18]. Negatively stained electron microscopy and cryo-electron microscopy studies have documented that intact phycobilisomes consist of multiple cylindrical antennae units structurally distributed into the core and the rods [19–23]. Fig. 1 schematically illustrates the most commonly reported "tricylindrical core and six rods" model for the phycobilisomes [7,24]. While PEs occupy the tip of the antennae rods, CPCs are invariably positioned at the base region adjacent to the APC core. Appropriate linker polypeptides that occupy the central channel of the antenna rods structurally cement individual disks

Abbreviations: CPC, C-phycocyanin; PE, Phycoerythrin; APC, Allophycocyanin; Syn, *Synechococcus* sp. PCC; F., Fremyella; PCB, Phycocyanobilins; S., Spirulina; D, Donor; A, Acceptor; PDB, Protein Data Bank

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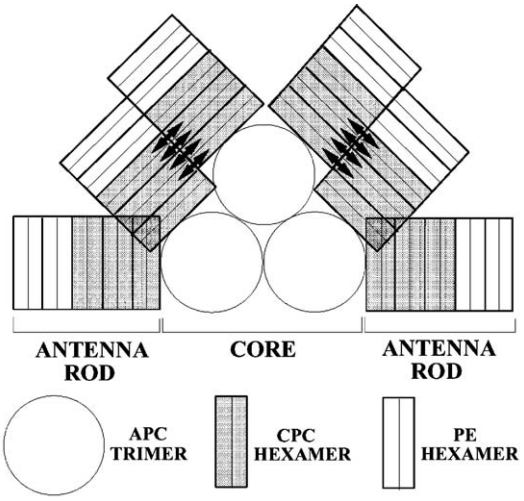

Fig. 1. Schematic sketch of "tricylindrical core and six rods" model of phycobilisome supramolecular assembly as suggested by electron microscopic studies [19–21,24]. The arrows indicate the directions of proposed lateral energy transfer between the two antenna rods involving adjacent CPC hexamer disks.

in the phycobilisome assembly. In addition, they interact with some chromophores, thereby tuning them, and in some cases, they carry their own chromophores participating directly in energy transfer. In all other cases, the physical coupling is the major factor that indirectly guarantees energetic coupling. Light energy transduces in the direction from tip to the core through PE → CPC → APC → Reaction Center with an overall quantum efficiency >95% [24].

In CPC, linear tetrapyrrole chromophores called phycocyanobilins (PCB), act as light absorbing centers. Three chromophores within an (αβ)-monomer, namely, α84, β84, and β155, are covalently attached to the apoprotein via thioether bonds to different cysteine residues. Although the three chromophores are chemically alike, the conformation and specific electrostatic interactions with the surrounding protein matrix modifies their spectroscopic properties. Accordingly, β155 is classified as a high-energy chromophore (λ_{max} = 596–600 nm), α84 being intermediate (λ_{max} = 618–624 nm), and β84 is the least (λ_{max} = 622–628 nm) energy absorber [7]. The α84 and β155 absorb light at the blue edge (short wavelength) of the spectrum and transfer the energy in a non-radiative fashion to the β84 at a slightly longer wavelength [25,26]. Antennae rods contain an array of spatially separated chromophores that absorb excitation via the α84 and β155 and cause depolarization resulting in energy hopping as a random walk (trap or diffusion limited) along the line of β84 within the rods. Specific structural organization of CPC hexamers is critical for the efficient excitation transfer [11,13].

The present study is motivated by our observation of a novel organization of two *S. platensis* CPC hexamer disks in close proximity within the crystal asymmetric unit [10] whose mutual association is not related by the crystal symmetry. We have estimated the rate of energy transfer for a set of all chromophore pairs within and between the two hexamers using the Förster equation. Based on this analysis, we present a quantitative model for inter-rod energy transfer in lateral direction between the adjacent CPC disks. The model is significant in the context of close association of CPC disks from adjacent rods near the core region of hemidiscoidal phycobilisome assembly (Fig. 1) as suggested by electron microscopic studies [19–23].

2. Materials and methods

According to Förster [27] the energy transfer rate employing the approximation of chromophore interactions as long-range dipole–dipole interaction for a pair of donor (D) and acceptor (A) chromophores is given by,

$$k_{DA} = \frac{9\ln 10}{128\pi^5 N_A n^4} \frac{\varepsilon_A}{\tau_D^o} \frac{k_{DA}^2}{R_{DA}^6} \frac{\int_0^\infty F_D(\lambda) A_A(\lambda) \lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda} \quad (1)$$

The terms involved in the above equation are as follows: N_A, the Avogadro number, and n (=1.33), the refractive index are the constants. Moog et al. [28] have reported the appropriate value for the refractive index in Eq. (1) as that of bulk solvent (1.33) and reflects the diluted protein solution environment. The value of n used in this study is consistent with the findings by Debreczeny et al. for the calculation of transfer rates in *Synechococcus sp*. PCC 7002 (formerly *Agmenellum quadruplicatum*) CPC monomers and trimers [29,30].

The variables used in the above expression include ε_A, the maximum visible molar absorptivity of the acceptor chromophore and τ_D^0, the intrinsic fluorescence lifetime of donor chromophore. Principal parameters that govern the rate of excitation transfer are (1) R_{DA}, the distance of separation as defined between the center of mass of the (π-conjugated) atoms of the donor and acceptor chromophore pairs (2) κ_{DA}, the orientation factor that depends on the relative orientation of the unit vectors describing the direction of chromophore transition dipoles and (3) the integral term which determines the degree of overlap between fluorescence spectrum of the donor (F_D) with absorption spectrum of the acceptor (A_A).

Well-defined electron density from our crystal structure has led to complete modeling of all the chromophores, determine their conformation, and perform the calculations to obtain different parameters to a good accuracy. The parameters R_{DA} and κ_{DA} were calculated using the chromophore coordinates of *S. platensis* CPC structure determined in our laboratory (Protein Data Bank Code: 1HA7; http://www.rcsb.org/pdb). The values of maximum visible molar absorptivity (ε), the intrinsic fluorescence lifetime (τ^0), and overlap integrals were obtained from the experimental results of pico-second time resolved fluorescence spectrometry on monomeric CPC from *Syn*. 7002 [29,30]. We expect minimal variation between the spectroscopic parameters of monomeric CPC from *S. platensis* and *Syn*. 7002 because the conformation and electrostatic interactions of chromophores are completely conserved with the surrounding protein matrix that is responsible for their spectral properties [10].

The direction of chromophore transition dipoles is approximated by fitting a least square line to its π-conjugated atoms determined by the crystal structure. The orientation factor can then be calculated as

$$\kappa_{DA} = \mathbf{e_D} \cdot \mathbf{e_A} - 3(\mathbf{e_D} \cdot \mathbf{n_{DA}})(\mathbf{e_A} \cdot \mathbf{n_{DA}}) \quad (2)$$

where $\mathbf{e_D}$ and $\mathbf{e_A}$ are the unit vectors corresponding to the direction of donor and acceptor chromophores and $\mathbf{n_{DA}}$ is the direction of the line joining the centroids of chromophores. The energy transfer rates are depicted in terms of "transfer time" (τ_t, also called equilibration time), which is an inverse of the sum of forward and reverse rates $1/(k_{DA}+k_{AD})$. τ_t is an appropriate parameter that can be validated experimentally using pico- or femto-second fluorescence spectroscopy techniques [31,32].

3. Results and discussion

We have applied the Förster mechanism to the two adjacent hexameric CPC molecules as reported in the crystal structure of *S. platensis* CPC determined in our laboratory, at 2.2 Å resolution with an agreement factor (R_{cryst}) of 19.2% [10]. The lateral association of two CPC molecules as observed in the

asymmetric unit presents a novel organization that is explored in this study for modeling inter-rod excitation transfer routes. It has been documented that there exists two additional modes of hexamer packing in lateral direction generated from crystallographic symmetry operation [15]. The association of two hexamers as in the asymmetric unit of our *S. platensis* CPC structure (PDB Code: 1HA7) results an interface area of 1682 Å^2 which is significantly higher than the other interfaces generated by crystallographic symmetry considerations (~800 Å^2). These values compare well with the known protein–protein complexes where the burial of solvent accessible molecular surface area of 1600 (±400) Å^2 corresponds to a standard interface size [33]. Considering the distance between chromophores and buried surface areas between the three forms of associations, we deduce that the mode of hexamer interactions observed within the asymmetric unit is relatively favorable for the association as well as inter-rod energy transfer and the same is reported in detail.

The applicability of the Förster's Eq. (1) requires the condition of weak coupling between chromophores. In monomeric CPC from *S. platensis*, chromophores are well separated with the shortest distance between the centroids of any pair being >20 Å (see Supplementary data, Table 1) thus resulting in excitation being localized on one chromophore at a time. The absorption spectrum of the whole system therefore can be treated as the sum of its components [27]. This assumption is supported by a recent analysis that compares the absorption and fluorescence measurements for each type of PCBs (α84, β84 and β155) between isolated subunits (α, β, αβ) and a mutant (αβ)-subunit where β155 PCB is absent [32]. Their study has revealed that the absorption spectrum of three chromophores act additively in the monomeric forms of CPCs due to the weak coupling of PCB chromophores. Furthermore, applicability of the Förster mechanism with the weak coupling approximation has been validated with a good agreement of calculated transfer rates to the spectroscopic measurements of CPC subunits isolated from *Syn.* 7002 and *Mastigocladus laminosus* [29,30,34].

In addition to the atomic resolution and quality of the X-ray structure, the accuracy of energy transfer rate estimates depend on the form of the Förster equation used for this calculation. An approximation of the Förster equation, $k_{DA}=(k_{DA}^2/\tau^0)(R_0/R_{DA})^6$ where R_0 (=50 Å), the Förster radius is frequently used in calculating the energy transfer rates [11–14,17]. Comparing with Eq. (1) that is used in this study, the above equation neglects the variable integral term that determines the degree of overlap between fluorescence spectra and estimates into a constant R_0. The above equation also approximates the intrinsic fluorescence contributions from each type of chromophore by assigning an overall value of $\tau^0=1.9$ ns. Debreczeny et al. have documented that for CPC monomers and trimers from *Syn.* 7002, the rate calculations based on Eq. (1) result in better agreement with the experimental measurements [29,30]. Similar mismatch between experimental measurements and calculated rate transfer values that use the above approximation for the Förster equation were seen in the case of *M. laminosus* [34]. Therefore, we have adopted Eq. (1) for calculation of transfer rates for the *S. platensis* CPC that we believe almost certainly enhances the accuracy of our estimates.

For comparison, energy transfer parameters for all possible 153 pairs of dipolar transitions within the $(\alpha\beta)_6$-hexamers of *S. platensis* CPC were calculated. The calculations indicate that 63 pairs of chromophores per hexamer have transfer rates exceeding 1 ns^{-1} (30 pairs among them have $k_{DA}>10$ ns^{-1}, see Supplementary data, Table 1) that is rapid compared with the fluorescence life times of chromophore excited states. Within the limits of variation that is observed for CPCs from diverse species, the estimated values of orientation factor magnitudes ($|\kappa|$) for different chromophores correlate with the documented values of *Syn.* 7002, *M. laminosus*, *Cyanidium caldarium*, and *Synechococcus elongatus* [11,17,35]. Transfer rates determined for *S. platensis* CPC monomer and trimer subunits (see Supplementary data, Fig. 1 and Table 1 for details) are comparable with experimental measurements on CPC oligomers from *Syn.* 7002 and *M. laminosus*. The formation of higher order assembly from trimers into hexamers and stacking of hexamers into rods is responsible for coupling chromophores from adjacent hexamers within suitable distances and orientations that result in formation of additional pathways for intra-rod excitation transfer [11,13].

The possibility of lateral energy transfer between adjacent hexamers has been suggested by us [10] and others [11,12,15,16] as a model for inter-rod energy transfer. However, quantitative estimates of transfer rates have not been carried out so far. We have examined the structure for the energy transfer between the hexamers in lateral direction. Of all the 324 possible combinations of chromophore pairs in two hexamers, ten paths have significantly high transfer rates. The calculated energy transfer parameters for the ten pairs are presented in Table 1. All the pairwise transitions involve the peripheral β155 chromophore. This is because the unique form of hexamer association brings the peripheral β155 chromophores from adjacent CPC disks to close proximity of distances <30 Å (Fig. 2, Table 1). The estimated τ_t for the pair 4β155 ↔ 5′β155 is 4 ps leading to an ultra-fast transfer path between adjacent hexamers. Similarly, the paths 1β155 ↔ 3′β155, 4β155 ↔ 3′β155, and

Table 1
Relative distances (in Å), orientation factors κ_{DA}, forward and reverse Förster transfer rates k_{DA}, k_{AD} (in ns^{-1}) and transfer time τ_t (in ps) between the adjacent hexamers

Hexamer 1–Hexamer 2	R_{DA} (Å)	κ_{DA}	k_{DA} (ns^{-1})	k_{AD} (ns^{-1})	τ_t (ps)[a]
4β155 ↔ 5′β155	20.42	0.44	121.90	121.90	4
1β155 ↔ 3′β155	29.82	0.75	36.68	36.68	14
4β155 ↔ 3′β155	21.28	0.16	13.14	13.14	38
1β155 ↔ 5′β155	21.81	0.13	7.69	7.69	65
4α84 ← 5′β155	40.06	0.85	1.75	11.62	75
4β155 → 5′α84	40.31	0.83	10.63	1.60	82
6β84 ← 5′β155	49.26	−1.31	0.63	6.17	147
4β155 → 4′β84	49.53	−1.29	5.74	0.58	158
1β155 → 2′β84	50.78	1.14	3.89	0.39	233
3β84 ← 3′β155	51.37	1.15	0.38	3.71	245

[a] Transfer time τ_t is calculated as $1/(k_{DA}+k_{AD})$. Only those chromophore pairs with significant energy transfer rates are listed. The location of these chromophores in the inter-hexamer interface is shown in Fig. 2.

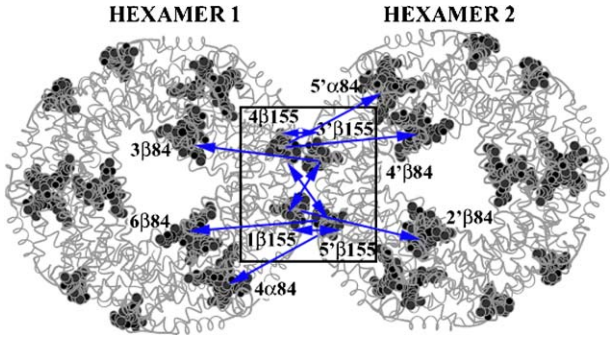

Fig. 2. Lateral energy transfer pathways between two *S. platensis* CPC hexamer disks. The molecular structure of two hexamers as determined from the crystal structure analysis is presented through an axis that is approximately perpendicular to the planes of the disks. Chromophores are shown in space filling representation and the protein matrix in coil representation. For clarity, only those chromophores listed in Table 1 are labeled. The arrows indicate the excitation transfer pathways for the respective chromophore pairs (see Table 1 for transfer times for indicated paths). The double-headed arrows indicate the resonance energy transfer between similar chromophores while the single headed arrows indicate the direction of downhill transfer between the dissimilar chromophores. The box drawn highlights the specific β155 chromophores responsible for mediating ultra-fast excitation transfers in the interface region of adjacent hexamer disks.

1β155 ↔ 5′β155 correspond to a fast transfer times of 14 ps, 38 ps, and 65 ps, respectively. Directional energy transfers are also possible from β155 of one hexamer to β84 of adjacent hexamer either directly or *via* α84 (Fig. 2, Table 1). We observe that the peripheral positioning of β155 chromophores is advantageous in providing additional lateral pathways for energy transfer via excitation coupling between the two adjacent CPC hexamers.

Mechanisms for intra-rod energy transfer between stacked hexamers along the antennae rods have been proposed earlier based on the observation of hexamer association in crystal unit cell [11–14]. For comparison, we have calculated the intra-rod transfer rates between the hexamers using Eq. (1) for three of the proposed paths for CPC from *Syn*. 7002 [11,12]. The shortest of the paths corresponds to a distance of 26 Å between a pair of β84 ↔ β84 chromophores with a transfer time of 8 ps (k_{DA} = 59.9 ns^{-1}). The transfer times for other two paths, α84 ↔ α84 and α84 → β84 are 122 ps and 186 ps, respectively. This in comparison with inter-rod energy transfer times (τ_t = 4–65 ps, see Fig. 2 and Table 1) indicates that the excitation transfer in the lateral direction may provide competitive alternative routes, if the hexamers associate in a fashion similar to that observed in the crystal structure.

The results obtained here are significant when considering the structural organization of the phycobilisome assembly. Based on the observations from the electron microscopy experiments, various models have been proposed for the supramolecular assembly of phycobilisomes [19–23,36]. Among the diverse cyanobacterial species, one of the most commonly reported phycobilisome model consists of tricylindrical core and six rods (Fig. 1) [7,24]. Deviations from this model are seen in terms of the number of cylindrical units present within the core, the rods, the angle of association between the rods, and the length of the rods in a few cases [22,36]. Nevertheless, a majority of the rods emanate radially in pairs out of the APC core assembly thereby suggesting that in a region around the APC core, the CPC disks from adjacent rods come in close proximity with resemblance to the association of CPC disks in the *S. platensis* crystal structure. In phycobilisomes that exhibit parallel or near parallel organization of rods, inter-rod energy transfers in combination with the established intra-rod pathways would contribute to the high efficiency of excitation transduction towards the core of the light-harvesting assembly.

The quantitative study presented here provides a testable model for the lateral energy transfers between CPC hexamer disks and supplements the existing energy transfer models of cyanobacterial light-harvesting systems. Low-resolution studies to date on *S. platensis* phycobilisome [37] have not been conclusive about the fine structure of the assembly. In addition to the proposed models reported in this study and elsewhere [11,12,15,16], further investigation by a battery of sophisticated experimental techniques, viz. ultra-fast time-resolved spectroscopy, cryo-electron microscopy would be necessary for a better understanding of the phycobilisome energetics.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.bbabio.2006.02.012.

References

[1] B.R. Green, W.W. Parson, Light-harvesting antennas in photosynthesis, vol. 13, Kluwer Academic Publishers, Hingham, MA, 2003.
[2] R.E. Blankenship, Molecular Mechanisms of Photosynthesis, Blackwell, Oxford, 2002.
[3] R. Huber, Nobel lecture. A structural basis of light energy and electron transfer in biology, EMBO J. 8 (1989) 2125–2147.
[4] X. Hu, K. Schulten, How nature harvests sunlight, Phys. Today 50 (1997) 28–34.
[5] R. van Grondelle, J.P. Dekker, T. Gillbro, V. Sündstrom, Energy transfer and trapping in Photosynthesis, Biochim. Biophys. Acta 1187 (1994) 1–65.
[6] V. Sundstrom, T. Pullerits, R. van Grondelle, Photosynthetic light-harvesting: reconciling dynamics and structure of purple bacterial LH2 reveals function of photosynthetic unit, J. Phys. Chem., B 103 (1999) 2327–2346.
[7] R. MacColl, Cyanobacterial phycobilisomes, J. Struct. Biol. 124 (1998) 311–334.
[8] Z. Liu, H. Yan, K. Wang, T. Kuang, J. Zhang, L. Gui, X. An, W. Chang, Crystal structure of spinach major light-harvesting complex at 2.72 Å resolution, Nature 428 (2004) 287–292.
[9] D. Gust, T.A. Moore, A.L. Moore, Mimicking photosynthetic solar energy transduction, Acc. Chem. Res. 34 (2001) 40–48.
[10] A.K. Padyana, V.B. Bhat, K.M. Madyastha, K.R. Rajashankar, S. Ramakumar, Crystal structure of a light-harvesting protein C-phycocyanin

from *Spirulina platensis*, Biochem. Biophys. Res. Commun. 282 (2001) 893–898.

[11] T. Schirmer, W. Bode, R. Huber, Refined three-dimensional structures of two cyanobacterial C-phycocyanins at 2.1 and 2.5 Å resolution. A common principle of phycobilin–protein interaction, J. Mol. Biol. 196 (1987) 677–695.

[12] T. Schirmer, R. Huber, M. Schneider, W. Bode, M. Miller, M.L. Hackert, Crystal structure analysis and refinement at 2.5 Å of hexameric C-phycocyanin from the cyanobacterium Agmenellum quadruplicatum. The molecular model and its implications for light-harvesting, J. Mol. Biol. 188 (1986) 651–676.

[13] M. Duerring, G.B. Schmidt, R. Huber, Isolation, crystallization, crystal structure analysis and refinement of constitutive C-phycocyanin from the chromatically adapting cyanobacterium Fremyella diplosiphon at 1.66 Å resolution, J. Mol. Biol. 217 (1991) 577–592.

[14] B. Stec, R.F. Troxler, M.M. Teeter, Crystal structure of C-phycocyanin from *Cyanidium caldarium* provides a new perspective on phycobilisome assembly, Biophys. J. 76 (1999) 2912–2921.

[15] X.Q. Wang, L.N. Li, W.R. Chang, J.P. Zhang, L.L. Gui, B.J. Guo, D.C. Liang, Structure of C-phycocyanin from *Spirulina platensis* at 2.2 Å resolution: a novel monoclinic crystal form for phycobiliproteins in phycobilisomes, Acta Crystallogr., D Biol. Crystallogr. 57 (2001) 784–792.

[16] N. Adir, R. Vainer, N. Lerner, Refined structure of C-phycocyanin from the cyanobacterium *Synechococcus vulcanus* at 1.6 Å: insights into the role of solvent molecules in thermal stability and co-factor structure, Biochim. Biophys. Acta 1556 (2002) 168–174.

[17] J. Nield, P.J. Rizkallah, J. Barber, N.E. Chayen, The 1.45 Å three-dimensional structure of C-phycocyanin from the thermophilic cyanobacterium *Synechococcus elongatus*, J. Struct. Biol. 141 (2003) 149–155.

[18] L.K. Anderson, C.M. Toole, A model for early events in the assembly pathway of cyanobacterial phycobilisomes, Mol. Microbiol. 30 (1998) 467–474.

[19] E. Gantt, C.A. Lipschultz, B. Zilinskas, Further evidence for a phycobilisome model from selective dissociation, fluorescence emission, immunoprecipitation, and electron microscopy, Biochim. Biophys. Acta 430 (1976) 375–388.

[20] D.A. Bryant, G. Guglielmi, N. Tandeau de Marsac, A.M. Castets, G. Cohen-Bazire, The structure of cyanobacterial phycobilisomes: a model, Arch. Microbiol. 123 (1979) 113–127.

[21] A.N. Glazer, R.C. Williams, G. Yamanaka, H.K. Schachman, Characterization of cyanobacterial phycobilisomes in zwitterionic detergents, Proc. Natl. Acad. Sci. U. S. A. 76 (1979) 6162–6169.

[22] A. Ducret, W. Sidler, E. Wehrli, G. Frank, H. Zuber, Isolation, characterization and electron microscopy analysis of a hemidiscoidal phycobilisome type from the cyanobacterium *Anabaena* sp., PCC 7120, Eur. J. Biochem. 236 (1996) 1010–1024.

[23] Z.W. Yi, H. Huang, T.Y. Kuang, S.F. Sui, Three-dimensional architecture of phycobilisomes from *Nostoc flagelliforme* revealed by single particle electron microscopy, FEBS Lett. 579 (2005) 3569–3573.

[24] A.N. Glazer, Light guides. Directional energy transfer in a photosynthetic antenna, J. Biol. Chem. 264 (1989) 1–4.

[25] R.E. Dale, F.W. Teale, Number and distribution of chromophore types in native phycobiliproteins, Photochem. Photobiol. 12 (1970) 99–117.

[26] A.N. Glazer, Light harvesting by phycobilisomes, Annu. Rev. Biophys. Biophys. Chem. 14 (1985) 47–77.

[27] T. Förster, Mechanisms of energy transfer, in: M. Florkin, E.H. Stotz (Eds.), Comprehensive Biochemistry, vol. 22, Elsevier, Amsterdam, 1967, pp. 61–80.

[28] R.S. Moog, A. Kuki, M.D. Fayer, S.G. Boxer, Excitation transport and trapping in a synthetic chlorophyllide substituted hemoglobin: orientation of the chlorophyll S1 transition dipole, Biochemistry 23 (1984) 1564–1571.

[29] M. Debreczeny, K. Sauer, J. Zhou, D.A. Bryant, Comparison of calculated and experimentally resolved rate constants for excitation energy transfer in C-phycocyanin. Part I: monomers, J. Phys. Chem. 99 (1995) 8412–8419.

[30] M. Debreczeny, K. Sauer, J. Zhou, D.A. Bryant, Comparison of calculated and experimentally resolved rate constants for excitation energy transfer in C-phycocyanin: Part II. trimers, J. Phys. Chem. 99 (1995) 8420–8431.

[31] G.R. Fleming, R. van Grondelle, Femtosecond spectroscopy of photosynthetic light-harvesting systems, Curr. Opin. Struct. Biol. 7 (1997) 738–748.

[32] M. Debreczeny, K. Sauer, J. Zhou, D.A. Bryant, Monomeric C-phycocyanin at room temperature and 77 K: resolution of the absorption and fluorescence spectra of the individual chromophores and the energy transfer rate constants, J. Phys. Chem. 97 (1993) 9852–9862.

[33] L. Lo Conte, C. Chothia, J. Janin, The atomic structure of protein–protein recognition sites, J. Mol. Biol. 285 (1999) 2177–2198.

[34] A.A. Demidov, M. Mimuro, Deconvolution of C-phycocyanin β-84 and β-155 chromophore absorption and fluorescence spectra of cyanobacterium *Mastigocladus laminosus*, Biophys. J. 68 (1995) 1500–1506.

[35] K. Brejc, R. Ficner, R. Huber, S. Steinbacher, Isolation, crystallization, crystal structure analysis and refinement of allophycocyanin from the cyanobacterium *Spirulina platensis* at 2.3 Å resolution, J. Mol. Biol. 249 (1995) 424–440.

[36] M. Glauser, D.A. Bryant, G. Frank, E. Wehrli, S.S. Rusconi, W. Sidler, H. Zuber, Phycobilisome structure in the cyanobacteria *Mastigocladus laminosus* and *Anabaena* sp. PCC 7120, Eur. J. Biochem. 205 (1992) 907–915.

[37] C. Chen, Y.Z. Zhang, X.L. Chen, B.C. Zhou, H.J. Gao, Langmuir–Blodgett film of phycobilisomes from blue-green alga *Spirulina platensis*, Acta Biochim. Biophys. Sin. (Shanghai) 35 (2003) 952–955.