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藻类捕光天线系统: 结构与功能的统一

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摘要: 藻类是光合自养的水生孢子植物, 为了适应水下弱光的特殊生境, 藻类捕光天线历经亿万年的进化, 形成了特殊的结构与功能。从发现藻类捕光天线的存在到至今的 70 多年间, 其结构解析技术的发展共经历了 4 个阶段: 首先是利用生化及普通光谱技术研究结构组成 (1950−1980 年); 其次是利用 X-ray 晶体学技术研究局部精细结构 (1980 年至今); 再次是利用电镜技术研究完整的粗略结构 (1980−2010 年); 最后是近 10 年来利用冷冻电镜技术研究完整的精细结构 (2010 年至今)。目前以蓝藻、红藻、绿藻和硅藻为主的藻类捕光天线复合体完整的精细结构均已被解析, 仅 2019 年就有 10 余种精细结构被发现。藻类捕光天线系统结构生物学的研究, 不仅搭建了对结构与功能统一认识的桥梁, 而且为深入揭示藻类光合作用高效能量传递机制奠定了坚实的结构基础。将藻类捕光天线系统结构和功能统一起来, 进一步研究对光环境的适应性成为未来的重点, 并将为藻类捕光天线蛋白在光电器件领域的应用提供充分的科学依据。

关键词: 藻类; 捕光天线系统; 结构生物学; 结构解析技术; 高效能量传递; 光适应

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1 引言

藻类是光合自养的水生孢子植物, 是地球上最原始的进行放氧光合作用的植物, 可分为原核藻类及真核藻类。原核藻类的成员主要为蓝藻, 它通过内共生进化出各种真核藻类。最初, 蓝藻的初级内共生演化出 3 个分支: 灰胞藻、红藻及绿藻[1]。随后, 红藻及绿藻通过一系列次内共生产生了其他的真核藻类[2]。按照传统方法, 真核藻类通常被分为 10 个门: 绿藻门、轮藻门、裸藻门、红藻门、隐藻门、甲藻门、金藻门、黄藻门、硅藻门及褐藻门[3]。

藻类可在各类地球环境中(湖泊、海洋、温泉、高山、极地等)生存, 特别是水下弱光环境造就了藻类独特而高效的捕光能力[4]。为了适应各种光环境, 藻类进化出了各种捕光天线(色素−蛋白复合体), 包括定位于类囊体膜外的水溶性复合体, 以及在类囊体膜内的疏水性复合体。这些复合体可通过调整其结合色素的数量、种类及位点, 吸收环境中特定波段的光[5]。例如水溶性捕光天线复合体藻胆体(Phycobilisome, PBS), 可通过共价结合的各类藻胆素, 如藻蓝胆素(Phycocyanobilin, PCB)、藻红胆素(Phycoerythrobilin, PEB)、藻尿胆素(Phycourobilin, PUB)和藻紫胆素(Phycoviolobilin, PVB)等吸收 460～670 nm 的可见光[6]; 膜蛋白捕光天线复合体(Light-harvesting Complex, LHC)可通过非共价结合的各类色素如叶绿素

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(Chlorophyll, Chl), 及各种类胡萝卜素(Carotenoids)如岩藻黄素(Fucoxanthin, Fx)、甲藻黄素(Diadinoxanthin, Dd)和硅藻黄素(Diatoxanthin, Dt)等吸收 350～750 nm 的光[7–8], 这些吸收的光能被捕光天线复合体以大于 90% 的效率传递至光合反应中心。在此过程中, 类胡萝卜素可以通过淬灭激发态叶绿素的方式进行光保护。这些捕光和传能的过程之所以如此的高效, 与藻类捕光天线独特的蛋白结构密不可分[9–13]。

藻类拥有的独特的捕光天线结构是其行使捕光和传能过程的基础(表 1)[14–16], 研究藻类捕光天线的精细结构具有非常重要的意义。其精细结构的揭示, 可以帮助人们了解天线的捕光和传能机制, 并为光电仿生器件提供重要的结构和功能基础[17], 这对开发太阳能电池甚至人工光合作用的合成都至关重要。

但需要注意的是, 藻类捕光天线结构生物学的发展非常依赖于相关的检测及解析技术。这些技术被用来分析藻类捕光天线的成分和结构, 是影响结构分辨率的重要因素, 因此相关的研究方法学和技术手段的进步至关重要。本文将以研究方法学和技术手段的进步为线索, 回顾过去 70 年藻类捕光天线结构生物学的研究历程, 阐明结构生物学揭示的藻类捕光复合体结构与功能的统一性及其科学意义, 并展望有关领域未来发展趋势。

2　藻类捕光天线结构解析

2.1　生化提取和成分分析阶段

生化提取是解析藻类捕光天线结构的第一步, 也是后续成分分析的重要基础。自 20 世纪 50 年代起, 人们开始通过简单易行的生理生化技术, 广泛研究藻类捕光天线的组成及结构[18–20]。例如, Gantt 和 Lipschultz[21] 开发了从单细胞红藻紫球藻中分离完整 PBS 的方法, 大大推动了当时甚至后续的 PBS 结构的研究进展。后续提取完整 PBS 的方法均由此衍生而来, 至今仍延用了其中的经典条件及步骤, 例如细胞破碎缓冲液磷酸根浓度为 0.6～1.0 mol/L、pH 约为 7, 提取温度在 18°C 左右, 纯化方法选择蔗糖梯度离心法等[22–25]。

随后 Gingrich 等[26–28] 通过改进该方法, 分离纯化了蓝藻的 PBS, 例如聚球藻 *Synechococcus* PCC 6301、*Synechococcus* PCC 7002 等, 并通过蛋白电泳、吸收光谱及荧光发射光谱, 对 PBS 的蛋白成分及色素成分进行了鉴定(表 1)。基于这些研究成果, Glazer[29] 构建了聚球藻 *Synechococcus*6 701 藻胆体结构的初始模型。在完整的藻胆体结构被结构生物学研究技术解析之前, 该初始模型的建立对于分析藻胆体能量传递途径具有重要的指导意义。

2.2　利用 X-ray 解析晶体局部精细结构

X-ray 晶体学是解析藻类捕光天线复合体精细结构的第一选择[30](表 1)。蛋白本身的特性往往决定了其结晶的难易程度, 因此水溶性捕光天线和膜蛋白捕光天线的晶体结构解析进展并不对等。大量易结晶的水溶性捕光天线蛋白以及组成 PBS 的各类藻胆蛋白率先获得了原子分辨率的结构, 例如多甲藻素叶绿素蛋白(Peridinin-chlorophyll-protein, PCP)(2 Å)[31]、藻红蛋白(phycoerythrin, PE)(1.85 Å)[32]、藻蓝蛋白(phycocyanin, PC)(1.35 Å)[33] 和隐藻 PE545(0.97 Å、1.63 Å)[34–35] 等(表 2)。

由于膜蛋白纯化及结晶均较为困难, 因此获得 LHC 家族成员的晶体结构往往需要漫长的摸索过程。幸运的是, 目前已经获得了多种 LHCII、FCP(Fx and Chl *a*/*c* binding protein)的高分辨晶体结构(表 2), 这些结构清晰地展示了色基类型及结合位点[36–38]。大量晶体结构的成功解析, 为后续冷冻电镜三维重构计算奠定了重要的结构基础。

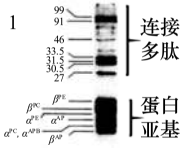
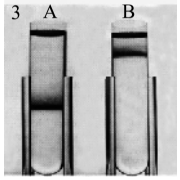
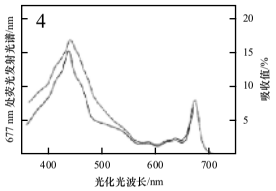
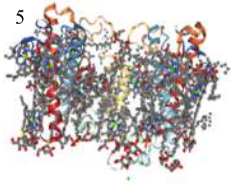
然而, 由于 LHC 家族成员的结构多样性, 膜蛋白又较难结晶, 因此大多数藻类的膜蛋白捕光天线的精细结构尚未通过 X-ray 晶体学方法获得(表 2)。此外, 超分子捕光复合体的结构也很难通过 X-ray 晶体学方法获得。一方面是由于超分子复合体的体积太大, 增加了结晶难度, 例如 PSI(photosystem I)-LHCI, PSII-LHCII 等大体积复合物至今未见晶体结构, 而其包含的体积小的 PSI、PSII 以及部分 LHC却早已通过结晶法获得精细结构[37, 39–40]; 另一方面是受限于复合体的体外理化性质, 例如 PBS 不仅体积大, 而且在体外易解聚, 很难通过结晶获得完整的精细结构。由于 X-ray 晶体学技术几乎没有机会完成部分藻类捕光天线的结构解析, 因此开发更多的结构解析技术变得非常必要。

2.3　利用电镜技术解析捕光天线复合体结构(以冷冻电镜为技术分水岭)

电镜技术一直是生物分子结构生物学结构解析, 特别是超大分子解析的重要手段, 只不过早期的解析清晰度远远不如 X-ray 晶体解析技术, 制约了技术的应用范围。早在 20 世纪 80 年代起, 人们便开始利用各种电镜技术对捕光天线的结构进行观察(表 1, 表 3), 例如通过透射电子显微镜(Transmission Electron Microscope, TEM)[21,68]、扫描隧道显微镜(Scanning Tunneling Microscope, STM)[69] 以及原子力显微镜(Atomic Force Microscope, AFM)[70] 观察到了各种不同类型

表 1　藻类捕光天线复合体粗略结构及精细结构

Table 1　Contour model and fine structures of algal light-harvesting antenna complexes

捕光天线类型	粗略结构鉴定方法	结构结果	与功能的关系	引用文献	精细结构鉴定方法	结构结果	与功能的关系	引用文献
PBS	生理生化+光谱技术	蛋白凝胶电泳鉴定藻胆体由藻胆蛋白及各种连接多肽组成；光谱测量藻胆体光吸收范围为460～700 nm 1  	揭示捕光范围及可能的能量传递路径	[29]	X-ray	藻胆蛋白脱辅基蛋白结构、结合色素类型及色素结合位点 2 	通过结合色素类型及结合方式预测能量传递路径	[41]
	普通电镜	PBS结构具有多样性，如半椭圆形、块状等	结合藻类生境，对比多种PBS形状及粗略结构，可揭示PBS形状与周围光环境的适应规律	[21]	冷冻电镜	PBS完整结构及细节结构，如各类连接蛋白组成的骨架形式；色素网络及色素结合位点	揭示PBS组装机制及能量传递途径	[42]
LHC及其与光系统的复合物	生理生化+光谱技术	蛋白凝胶电泳鉴定LHC蛋白大小及部分超分子复合体含有LHC的数量；光谱测量LHC光吸收范围为350～700 nm 3  4  	揭示捕光范围	[43]	X-ray	脱辅基蛋白结构、结合色素类型及色素结合位点 5 	揭示内部能量传递路径	[36]
	普通电镜	超分子复合体可能的组成成分，例如观察不同藻类的PSII-LHCII复合体中LHC的排列方式及数量	通过LHC与光合反应中心的结合方式推测可能的能量传递方式	[44]	冷冻电镜	复合体完整精细结构	能量传递途径及光保护机制	[45]

注：图片1引自文献[29]。图片1：SDS-聚丙烯酰胺凝胶电泳-*Synechococcus* PCC 6701的PBS多肽。图片2：隐藻（*Chroomonas* sp. CCMP270）捕光天线PC645晶体结构，结构下载于PDB（http://www.rcsb.org/），PDB码：4LMS，分辨率为1.35 Å。图片3和图片4引自文献[43]。图片3：褐藻Fx and Chl *a*/*c* binding protein A (FCPA)提取图；A：Triton-X-100样品提取处理；B：蔗糖梯度（0.2～0.5 mol/L蔗糖）样品分离。图片4：褐藻FCPA吸收光谱（波长450 nm处的上方线）及荧光发射光谱（波长450 nm处的下方线）的对比图。图片5：硅藻捕光天线FCP晶体结构，结构下载于PDB（http://www.rcsb.org/），PDB码为6A2W，分辨率为1.8 Å。

表 2　藻类捕光天线复合体晶体结构解析进展

Table 2　Progress in crystal structure analysis of algal light-harvesting antenna complexes

藻类	PSII主要捕光天线	PSI主要捕光天线	结合色素	文献
蓝藻	PBS: APC*, PC*, PE*, PEC (phycoerythrocyanin)*	IsiA (Iron-stress-induced protein)	PCB, PEB, PUB, PVB, Chl *a*	[26, 46−48]
红藻	PBS: APC*, PC*, PE*	LHCR: Lhcr	PCB, PEB, PUB, Chl *a*	[5, 21, 49−51]
绿藻	LHCII: Lhcb1-3, CP24, CP26, CP29*	LHCI*: Lhca	Chl *a*, Chl *b*	[52−54]
隐藻	Cr(Cryptophytes)-PBP (phycobiliprotein): Cr-PC*/Cr-PE*; LHC: Lhcr, Lhcz	同PSII	PCB, PEB, MBV(mesobiliverdin), DBV(dihydrobiliverdin), bilin 584, bilin 618, Chl *a*, Chl *c*, alloxanthin	[55]
硅藻	FCP*: Lhcf, Lhcx	同PSII	Chl *a*, Chl *c*, Fx, Dt, Dd	[56−58]
褐藻	FCP: Lhcf, Lhcr, Lhcx, Lhcz	同PSII	Chl *a*, Chl *c*, Fx,violaxanthin, zeaxanthin, Dt, Dd	[43, 58−59]
甲藻	PCP*; LHC: Lhcr, Lhcf, Lhcx	同PSII	Chl *a*, Chl *c*, Fx, violaxanthin	[60−61]
黄藻	XLH (Xanthophyceae light-harvesting complex) II	XLHI	Chl *a*, Chl *c*, Dd, Dt	[62]
金藻	LHC	LHC	Chl *a*, Chl *c*, Fx, violaxanthin	[63−64]
裸藻	LHC	LHC	Chl *a*, Chl *b*, neoxanthin, Dt, Dd, β-carotene	[65−67]
轮藻	LHC	LHC	Chl *a*, Chl *b*, α-carotene, β-carotene, γ-carotene, lutein, eaxanthin, neoxanthin, zeaxanthin, violaxanthin,	[65−67]

注: *代表已有高分辨晶体结构。

表 3　电镜技术解析藻类捕光复合体结构的研究进展

Table 3　Advance in electron microscope analysis of algal light-harvesting complexes

藻类	捕光天线复合体	电镜	冷冻电镜	解析分辨率(冷冻电镜)	引用文献
蓝藻	IsiA-PSI	√	√	3.5 Å	[76, 80]
	PBS	√		13 Å	[25]
	PBS_{rod}-PSI	√		–	[81]
	PBS-PSII	√		–	[82−83]
红藻	PSI-LHCI		√	3.82 Å	[74]
	PBS		√	3.5 Å, 2.82 Å	[22, 42]
绿藻	PSI-LHCI		√	3.49 Å, 2.9 Å	[75, 84]
	PSII-LHCII		√	3.2 Å	[85]
	C2S2-type PSII-LHCII		√	2.7 Å	[45]
	C2S2M2-type PSII-LHCII		√	3.2 Å	[86]
	C2S2M2N2-type PSII LHCII		√	3.7 Å	[74]
	C2S2M2L2-type PSII LHCII		√	3.4 Å	[45]
	PSI-LHCI-LHCII	√		–	[44]
硅藻	PSI-FCPI	√	√	–	[87−88]
	PSII-FCPII		√	3.02 Å, 3.8 Å	[78, 89]
隐藻	PSI-LHCI	√		–	[72]
黄藻	XLH	√		–	[71]

注: *代表已有高分辨晶体结构, √代表已用该技术进行了结构解析, –代表无分辨率报道。

的二维或三维 PBS 结构。部分膜蛋白捕光天线的结构也可通过电镜观察到，如体积较小的 XLH（来源于黄藻）[71] 以及大体积的 LHC 和光系统 I 的超分子复合物（如隐藻的 PSI-LHCI[72]、绿藻的 PSI-LHCI-LHCII[44] 等），结合已公布的晶体结构，可对这些负染图像进行三维重构计算，获得粗略结构模型。然而，由于这几种电镜技术本身的限制及获得的图像分辨率的限制，这些粗略结构相比于精细结构仅能提供复合体组成成分，丢失了大量的亚基及色基结构细节，例如 PBS 与 PSII-LHCII（图 1A，图 1C）的粗略结构，无法提供确切的亚基类型及空间位置，也无法观察到结合的色基，而精细结构（图 1B，图 1D）却可以提供这些细节。因此，直到冷冻电镜技术发展成熟之前，人们都很难通过电镜获得捕光天线复合体完整的精细结构。

冷冻电镜技术的应用不仅使结构生物学跨入了新时代，也使藻类捕光天线的结构解析得以关键性突破，这得益于冷冻电镜技术相比较 X-ray 结晶法对样品质量的依赖度更低[73]。仅 2019 年，便有 7 个超分子复合体的精细结构通过冷冻电镜技术获得[42, 45, 74−78]，

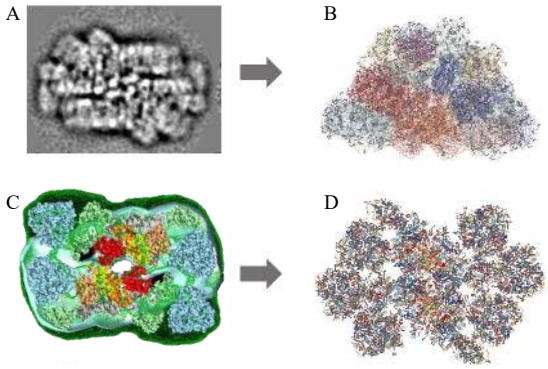


图 1 捕光复合体粗略结构及精细结构对比

Fig. 1 Comparison of contour and fine structures of algal light-harvesting complexes

A. 红藻（*Porphyridium cruentum*）PBS 电镜结构（粗略结构）（图片引自文献 [24]）；B. 红藻（*P. purpureum*）PBS 冷冻电镜精细结构（图片源于 PDB 库，PDB 码为 6KGX）；C. 豌豆 C2S2M2-type PSII-LHCII 电镜结构（粗略结构）（图片引自文献 [79]）；D. 绿藻（*Chlamydomonas reinhardtii*）C2S2M2N2-type PSII-LHCII 冷冻电镜精细结构（图片源于 PDB 库，PDB 码为 6KAF）

A. The rough structure of PBS from red alga *Porphyridium cruentum* by using electron microscope (picture quoted from reference [24]); B. the fine-structure of PBS from red alga *P. purpureum* by using cryo-electron microscope (PDB code is 6KGX); C. the electron microscope structure (rough structure) of C2S2M2-type PSII-LHCII from pea (picture quoted from reference [79]); D. the fine cryo-electron microscope structure of C2S2M2N2-type PSII-LHCII from *Chlamydomonas reinhardtii* (picture quoted from PDB library, PDB code is 6KAF)

包括提高了分辨率的 PBS 结构（红藻 *Porphyridium purpureum*，2.82 Å）[42]、绿藻的 PSI-LHCI 以及多种类型的 PSII-LHCII 等。这些结构清晰的揭示了复合体组件之间的连接与排布方式。目前，冷冻电镜技术在藻类捕光天线复合体结构解析领域的应用还有很大的发展空间。例如，利用冷冻电镜技术解析的藻类捕光天线复合体结构分辨率均未突破 2.5 Å（表 3）。因此，未来还需要对样品纯化以及冷冻电镜解析技术继续优化提升，以提高结构分辨率。

3 藻类捕光天线蛋白结构与功能的统一

结构生物学的进步，为深刻理解藻类捕光天线复合体的功能提供了大量结构细节，例如精细结构展示的大量的精准的发色团位置，提示了捕光天线系统内部高效的能量传递发生的可能机制。目前，将结构生物学与捕光天线功能整合为一体的研究方法学如下（图 2）。

（1）通过比对分析捕光蛋白的同源基因，结合其三维结构，揭示捕光蛋白结构与功能的进化关系。例如，在 2006 年，Zhao 和 Qin[90] 对藻胆蛋白同源基因进行了进化分析，发现某些藻胆蛋白中的部分氨基酸位点表现出较高的非同义替换率（图 2A），这些位点大多分布在发色团结合结构域和螺旋发夹结构域（X 和 Y）内或其附近（图 2B），并显示出共同进化的特征。将这些位点精确地定位在藻胆蛋白的三级结构上，发现脱辅基蛋白的发色团结合结构域为发色团创造了特定的微环境，以确保高效的能量转移效率[90]。这个研究从计算生物学的角度，证实了发色团与藻胆蛋白之间存在特定的空间环境以有效的进行共振能量转移。

（2）根据藻类捕光天线蛋白精细结构提供的发色团网络，预测能量传递的大概路径，并为利用超快时间分辨光谱研究能量传递提供结构基础。例如，通过硅藻（*Phaeodactylum tricornutum*）FCP 的结构解析发现，FCP 主要以二聚体的形式存在，且该结构揭示的 FCP 不仅结合了含氧光合作用生物中常见的 Chl *a*，而且结合了 Chl *c* 和 Fx，使它们能够捕捉蓝绿光以适应水中的光环境（图 3）[36]。随后通过 PSII-FCPII 的结构解析，进一步揭示了硅藻（*Chaetoceros gracilis*）FCPII 与 PSII 的连接方式及可能的能量传递模式。但是由于超分子复合体的结构过于复杂，具体的能量传递路径目前还不清晰[89]。由于复合体体积太大，色素分子

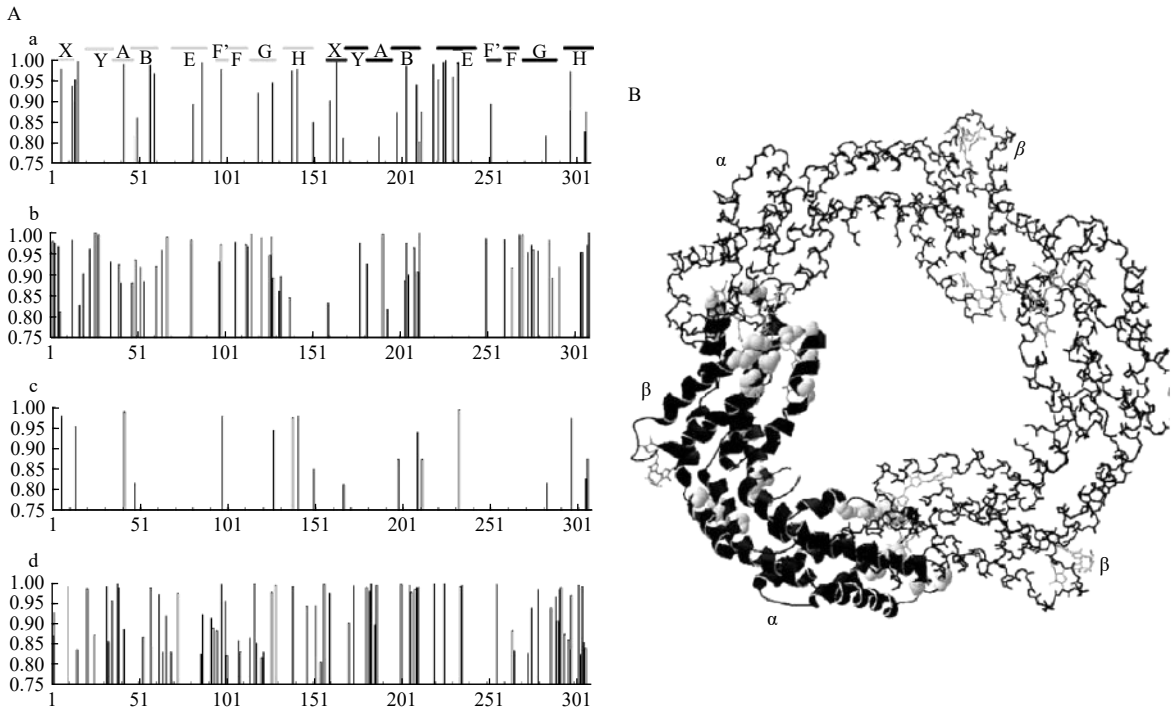


图 2　计算生物学分析蓝藻藻胆蛋白同源序列及结构[90]

Fig. 2　Computational biology analysis of cyanobacterial phycobiliprotein homologous sequence and structure [90]

A 为通过计算生物学比对蓝藻的藻胆蛋白同源序列, 识别非同义替换升高的位点 (后验概率大于 80%); 横轴为藻胆蛋白中的氨基酸排列位点; 纵轴为后验概率; A、B、E、F、F'、G、H 代表 7 个螺旋, X、Y 代表每个亚基 N 段的螺旋发卡域; 浅灰色为 α 亚基, 暗灰色为 β 亚基; 图内部的 a–d 分支分别为 PEC、PC、PE 和 APC。B 为蓝藻藻蓝蛋白三维结构; 灰色球状填充为 d*N*/d*S*(同义频率/非同义频率)替换比例升高的残基; 螺旋状条带表示蛋白质的 α 亚基和 β 亚基; 灰色杆状表示生色团

A represent alignment of cyanobacterial phycobiliprotein homologous sequences to identify sites with increased non-synonymous substitutions (posterior probabilities>80%); the horizontal axis is amino acid arrangement sites; the vertical axis is posterior probability; A, B, E, F, F', G, and H represent seven helices, X and Y represent the spiral hairpin domain at the N-terminus of each subunit; the gray lines represent α subunit, the dark gray lines represent β subunit; a-d represent PEC, PC, PE and APC, respectively. B represent three-dimensional structure of cyanobacterial phycocyanin; gray spheres represent the residues with increased synonymous frequency/non-synonymous frequency substitution ratio; helixes represent α subunit and β subunit; gray lines represent chromophore

较多而导致目前无法仅通过高分辨的复合体结构就准确预测能量传递路径的例子还有很多, 例如, 2020 年解析的来自紫球藻(*P. purpureum*)的 PBS 的结构, 包含了 1 598 个色素分子, 且 2.82 Å的分辨率足以使人们看清每个色基的结合位点[42]。然而, 由于色素数量庞大, 能量传递路径复杂, 其中可能涉及到多个激子能量传递, 甚至相干共振能量转移。因此, 准确的能量传递途径还需要配合各种精确的光谱技术手段进行分析。

(3)光谱学是分析捕光蛋白能量传递的最佳手段, 常用的有吸收光谱、荧光发射光谱、圆二色谱[91]以及超快光谱[92]。目前, 超快时间分辨光谱被认为是分析捕光蛋白能量传递机制的最佳光谱学手段, 超快时间分辨光谱可对飞秒(fs)内的能量传递过程进行监测[93–94]。例如, 二维超快时间分辨光谱显示, 隐藻捕光蛋白 PC645的两组色素分子之间存在振动相干节拍以及部分离域振动, 这使得能量转移速率增强[95–96]。

除了高效能量传递, 藻类捕光天线系统的精细结构, 为理解其光适应机制提供了更多的科学依据, 例如, 藻类捕光天线可通过结构的变化响应来启动各种光保护机制(如非光化学淬灭(NPQ)、状态转换等[97–98]), 以保护光合反应中心免受光损伤。例如, 发色团网络揭示的各类 LHC 的类胡萝卜素位置, 可辅助理解 LHC 的 NPQ 机制。近来, 有研究利用时间分辨红外光谱对 LHCII 的能量淬灭动力学及构象变化进行了分析[99], 该研究揭示了高等植物 LHCII 三聚体对多余激发能的耗散可响应温度和酸度的变化, 这可通过类胡萝卜素与叶绿素 612 之间的动态构象变化来调控。需要说明的是, 由于植物 LHCII 的结构与绿藻

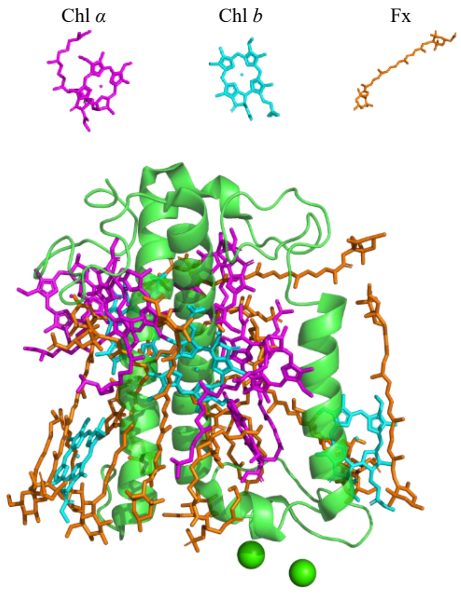


图 3 FCP 单体结构及其色素组成[36]

Fig. 3 Monomer structure and pigment composition of FCP [36]

硅藻(*P. tricornutum*)FCP 单体的结构信息来自 PDB 数据库(http://www.rcsb.org/), PDB 码为 6A2W

The structure of the FCP monomer from diatom *P. tricornutum* is provided by PDB database (http://www.rcsb.org/), PDB code is 6A2W

LHCII 的结构一样, 因此, 对高等植物 LHCII 的研究结果均可用来分析绿藻 LHCII。此外, 对高等植物 PSI-LHCI-LHCII 的精细结构解析, 也可帮助人们深入理解绿藻捕光天线的状态转换机制。通过对比绿藻中发现的各种类型的 PSII(photosystem II)-LHCII(C2S2-typePSII-LHCII、C2S2M2-typePSII-LHCII 及C2S2M2N2-typePSII-LHCII 等)复合体结构差异, 有助于深入理解 LHCII 对不同光条件下的响应机制[45, 74, 77, 86]。

藻类捕光天线的结构尽管可根据生活的光环境进行变化, 但是决定其结构类型的根本因素在于进化所决定的基因。因此, 尽管有一些藻类生活在相似的环境中, 但是其捕光天线结构却有差别, 例如都生活在海表面的单细胞蓝藻和红藻, 其具备的捕光天线结构并不相同。红藻的藻胆体较蓝藻藻胆体体积更大, 且红藻还具有膜蛋白 LHC[23, 42, 74]。因此, 藻类捕光天线的结构与功能的统一是建立在进化的基础上的, 解析不同藻类的捕光天线结构有助于理解藻类进化。

4 展望

冷冻电镜技术与超快时间分辨光谱技术的结合, 初步实现了对藻类捕光天线系统结构与能量传递功能的统一认识, 为深刻理解水生植物藻类为何具有高效的弱光捕获能力, 极高的传能效率以及灵活的光适应能力等, 奠定了坚实的结构基础。然而, 清晰绘制一幅特殊水环境如何塑造了特殊的捕光结构, 又如何获得高效而精准的捕光功能的系统画卷, 仍旧任重道远。

捕光天线结构中复杂的发色团网络结合各类光谱技术可揭示其高效的传能过程, 其中可用于解释两个相干量子系统引起的周期性振动过程的 CRET 机制引起了广泛的关注和争议。CRET 过程可使能量在几百飞秒内分布在整个系统(大于分子的直径)内[100], 因此部分观点认为相干共振能量转移是藻类捕光天线高效捕光的真正原因。然而, 也有部分观点认为该过程的相互作用时间太短暂, 在光合作用能量转移中没有任何功能意义[101]。而且, 通用的物理计算模型无法可靠的解释捕光天线内复杂的能量传递过程, 例如关于隐藻 PC645 中量子节拍的解释仍然备受争议, 因为原子振动也可呈现出相似的观测结果, 而这种观测结果很难区分是由哪种机制导致的[96]。因此, 需要开发更合理的计算模型(如非微扰计算模型)[102], 才能清楚地阐释相干能量传递机制是否是藻类捕光天线高效捕光的“杀手锏”。另外, 需要注意的是, 现今发现的捕光天线内的量子节拍大多数测量于 77 K, 而考虑到藻类生存的温度及温度升高对量子退相干过程的加剧作用, 在常温下测量量子相干的意义重大。

关于 PBS 光保护机制的研究还需要依赖相关复合物的结构解析。一方面, PBS 可通过橙色类胡萝卜素蛋白(water-soluble orange carotenoid protein, OCP)依赖型 NPQ 过程将多余的激发能进行热耗散(图 4a)。但关于 OCP 的结合位点仍存在争议, 虽然普遍认为活性 OCP 可以结合 PBS 的核心结构[103], 但至今没有相关的结构被解析, 无法直观的验证该观点。另一方面, PBS 可通过状态转换机制进行光保护, 其机制不同于膜蛋白 LHC(图 4)。为了避免 PSII 能量过强导致光损伤, 通常 PBS 可通过移动传能机制(图 4b, 状态一)和溢出机制(图 4b, 状态二)两种途径实现多余能量在光系统之间的重新分配[104]。遗憾的是, 至今, 两种机制的结构仅局限于结构模型, 直观的结构解析将寄希望于未来原位结构生物学技术的进步及动态结构研究方法的开发。

目前, 仍有许多藻类捕光天线的精细结构未被解析, 其中不乏有一些藻类拥有特殊结构的捕光天线。例如, 极端环境中的藻类为了在多变的光环境或不寻常的温度条件下, 依然能维持捕光天线的结构稳定性

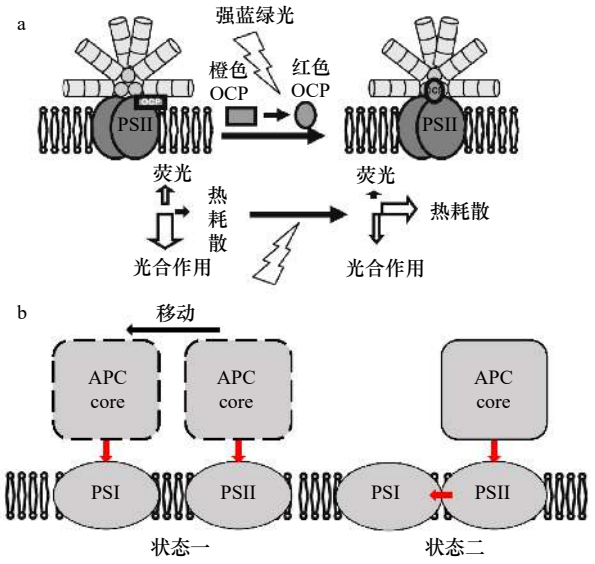


图 4　藻胆体光保护结构模型

Fig. 4　Photoprotective structural model of phycobilisomes

a. 藻胆体的 OCP 依赖型 NPQ 机制模型, 图片引自文献 [103]; b. 藻胆体状态转换模型, 状态一为移动传能机制, 状态二为能量溢出机制, 红色箭头为能量传递路径

a. The mechanism model of OCP-dependent NPQ in phycobilisomes, picture quoted from reference [103]; b. phycobilisome state transition model, state 1 represents mobile energy transfer mechanism, state 2 represents overflow mechanism, red arrow represents energy transfer path

和捕光效率, 进化出了独特的捕光天线结构。已发现嗜热蓝藻的捕光天线核结构中, 含有结构特殊的 PC (PC612), 可使藻胆体在高温条件结构依然稳定[105]; 南极红藻可通过转换不同的藻胆体类型来适应长期的光照环境和长期的黑暗环境[106]。但这些没有细节的粗略结构只是提供了理解适应机制的可能方向, 并不能辅助人们理解其特殊的捕光及传能机制。例如, 嗜热蓝藻中特殊结构的 PC 在藻胆体传能过程中的具体作用还不清楚; 驱动南极红藻两种藻胆体转换的具体机制以及两种藻胆体与光系统的联系仍未见报道。这些科学问题都需要通过解析精细结构, 甚至是动态光环境下的精细结构来解释。

现阶段, 藻类捕光天线系统结构生物学的研究已为深入揭示藻类光合作用高效能量传递机制奠定了坚实的结构基础, 验证了结构生物学揭示的藻类捕光复合体结构与其功能的统一性。此外, 通过特殊的捕光天线结构及其动态结构变化, 进一步研究捕光天线对光环境的适应性, 成为了未来的研究重点, 这将为藻类捕光天线蛋白在光电器件领域的应用提供科学依据。

参考文献:

[1] McFadden G I. Primary and secondary endosymbiosis and the origin of plastids[J]. Journal of Phycology, 2001, 37(6): 951−959.

[2] McFadden G I. Endosymbiosis and evolution of the plant cell[J]. Current Opinion in Plant Biology, 1999, 2(6): 513−519.

[3] 王寅初, 秦松. 真核藻类进化的研究进展与存在问题[J]. 生物学杂志, 2015, 32(3): 70−72.
Wang Yinchu, Qin Song. Evolution of eukaryotic algae: a mini-review of progress and problems[J]. Journal of Biology, 2015, 32(3): 70−72.

[4] Seckbach J. Enigmatic Microorganisms and Life in Extreme Environments[M]. Netherlands: Springer, 1999: 5775.

[5] Neilson J A D, Durnford D G. Structural and functional diversification of the light-harvesting complexes in photosynthetic eukaryotes[J]. Photosynthesis Research, 2010, 106(1/2): 57−71.

[6] Glazer A N. Light guides: Directional energy transfer in a photosynthetic antenna[J]. The Journal of Biological Chemistry, 1989, 264(1): 1−4.

[7] Krawczyk S, Krupa Z, Maksymiec W. Stark spectra of chlorophylls and carotenoids in antenna pigment-proteins LHC-II and CP-II[J]. Biochimica et Biophysica Acta (BBA)-Bioenergetics, 1993, 1143(3): 273−281.

[8] Büchel C. Fucoxanthin-chlorophyll-proteins and non-photochemical fluorescence quenching of diatoms[M] //Demmig-Adams B, Garab G, Adams III W, et al. Non-Photochemical Quenching and Energy Dissipation in Plants, Algae and Cyanobacteria. Dordrecht: Springer, 2014: 259−275.

[9] Mirkovic T, Ostroumov E E, Anna J M, et al. Light absorption and energy transfer in the antenna complexes of photosynthetic organisms[J]. Chemical Reviews, 2017, 117(2): 249−293.

[10] Onishi A, Aikawa S, Kondo A, et al. Energy transfer in Anabaena variabilis filaments under nitrogen depletion, studied by time-resolved fluorescence[J]. Photosynthesis Research, 2015, 125(1/2): 191−199.

[11] Li Wenjun, Su Hainan, Pu Yang, et al. Phycobiliproteins: Molecular structure, production, applications, and prospects[J]. Biotechnology Advances, 2019, 37(2): 340−353.

[12] Nelson N. Plant photosystem I—the most efficient nano-photochemical machine[J]. Journal of Nanoscience and Nanotechnology, 2009, 9(3): 1709−1713.

[13] 马建飞, 林瀚智, 秦松, 等. 蓝藻藻胆体的体外组装研究进展[J]. 中国科学: 生命科学, 2016, 46(9): 1054−1061.
Ma Jianfei, Lin Hanzhi, Qin Song. Advances in cyanobacterial phycobilisome assembling in vitro[J]. Scientia Sinica Vitae, 2016, 46(9):

1054−1061.

[14] Pu Yang, Zhu Guoliang, Ge Baosheng, et al. Photocurrent generation by recombinant allophycocyanin trimer multilayer on TiO_2 electrode[J]. Chinese Chemical Letters, 2013, 24(2): 163−166.

[15] Nagata M, Amano M, Joke T, et al. Immobilization and photocurrent activity of a light-harvesting antenna complex II, LHCII, isolated from a plant on electrodes[J]. ACS Macro Letters, 2012, 1(2): 296−299.

[16] 马建飞. 藻胆体的冷冻电镜三维重构及应用——以海洋红藻*Griffithsia pacifica*和嗜热蓝薄*Thermosynechococcus vulcanus*藻胆体为例[D]. 烟台: 中国科学院烟台海岸带研究所, 2015.
Ma Jianfei. 3-D reconstructions of phycobilisomes by cryo-electron microscopy and application—taking examples of phycobilisomes from the marine red alga *Griffithsia pacifica* and the thermophilic cyanobacterium *Thermosynechococcus vulcanus*[D]. Yantai: Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, 2015.

[17] Ma Jianfei, Chen Huaxin, Qin Song, et al. Applications of natural and artificial Phycobiliproteins in solar cells[J]. Current Biotechnology, 2015, 4(3): 275−281.

[18] Thornber J P, Sokoloff M K. Photochemical reactions of purple bacteria as revealed by studies of three spectrally different carotenobacteriochlorophyll-protein complexes isolated from Chromatium, strain D[J]. Biochemistry, 1970, 9(13): 2688−2698.

[19] Jones R F, Blinks L R. The amino acid constituents of the phycobilin chromoproteins of the red alga Porphyra[J]. The Biological Bulletin, 1957, 112(3): 363−370.

[20] Haxo F, O'hEocha C, Norris P. Comparative studies of chromatographically separated phycoerythrins and phycocyanins[J]. Archives of Biochemistry and Biophysics, 1955, 54(1): 162−173.

[21] Gantt E, Lipschultz C A. Phycobilisomes of *Porphyridium cruentum*. I. Isolation[J]. The Journal of Cell Biology, 1972, 54(2): 313−324.

[22] Zhang Jun, Ma Jianfei, Liu Desheng, et al. Structure of phycobilisome from the red alga *Griffithsia pacifica*[J]. Nature, 2017, 551(7678): 57−63.

[23] Arteni A A, Ajlani G, Boekema E J. Structural organisation of phycobilisomes from *Synechocystis* sp. strain PCC6803 and their interaction with the membrane[J]. Biochimica et Biophysica Acta (BBA)-Bioenergetics, 2009, 1787(4): 272−279.

[24] Arteni A A, Liu Luning, Aartsma T J, et al. Structure and organization of phycobilisomes on membranes of the red alga *Porphyridium cruentum*[J]. Photosynthesis Research, 2008, 95(2/3): 169−174.

[25] Yi Zhiwei, Huang Hui, Kuang Tingyun, et al. Three-dimensional architecture of phycobilisomes from *Nostoc flagelliforme* revealed by single particle electron microscopy[J]. FEBS Letters, 2005, 579(17): 3569−3573.

[26] Gingrich J C, Lundell D J, Glazer A N. Core substructure in cyanobacterial phycobilisomes[J]. Journal of Cellular Biochemistry, 1983, 22(1): 1−14.

[27] Myers J, Kratz W A. Relations between pigment content and photosynthetic characteristics in a blue-green alga[J]. The Journal of General Physiology, 1955, 39(1): 11−22.

[28] Yamanaka G, Glazer A N. Dynamic aspects of phycobilisome structure[J]. Archives of Microbiology, 1980, 124(1): 39−47.

[29] Glazer A N. Phycobilisomes[M]//Methods in Enzymology. Amsterdam: Elsevier, 1988: 304−312.

[30] Robinson C V, Sali A, Baumeister W. The molecular sociology of the cell[J]. Nature, 2007, 450(7172): 973−982.

[31] Hofmann E, Wrench P M, Sharples F P, et al. Structural basis of light harvesting by carotenoids: peridinin-chlorophyll-protein from *Amphidinium carterae*[J]. Science, 1996, 272(5269): 1788−1791.

[32] Camara-Artigas A, Bacarizo J, Andujar-Sanchez M, et al. PH-dependent structural conformations of B-phycoerythrin from *Porphyridium cruentum*[J]. The FEBS Journal, 2012, 279(19): 3680−3691.

[33] David L, Marx A, Adir N. High-resolution crystal structures of trimeric and rod phycocyanin[J]. Journal of Molecular Biology, 2011, 405(1): 201−213.

[34] Wilk K E, Harrop S J, Jankova L, et al. Evolution of a light-harvesting protein by addition of new subunits and rearrangement of conserved elements: crystal structure of a cryptophyte phycoerythrin at 1.63—A resolution[J]. Proceedings of the National Academy of Sciences of the United States of America, 1999, 96(16): 8901−8906.

[35] Doust A B, Marai C N J, Harrop S J, et al. Developing a structure-function model for the cryptophyte phycoerythrin 545 using ultrahigh resolution crystallography and ultrafast laser spectroscopy[J]. Journal of Molecular Biology, 2004, 344(1): 135−153.

[36] Wang Wenda, Yu Longjiang, Xu Caizhe, et al. Structural basis for blue-green light harvesting and energy dissipation in diatoms[J]. Science, 2019, 363(6427): eaav0365.

[37] Liu Zhenfeng, Yan Hanchi, Wang Kebin, et al. Crystal structure of spinach major light-harvesting complex at 2.72 Å resolution[J]. Nature, 2004, 428(6980): 287−292.

[38] Standfuss J, Van Scheltinga A C T, Lamborghini M, et al. Mechanisms of photoprotection and nonphotochemical quenching in pea light-harvesting complex at 2.5 Å resolution[J]. The EMBO Journal, 2005, 24(5): 919−928.

[39] Jordan P, Fromme P, Witt H T, et al. Three-dimensional structure of cyanobacterial photosystem I at 2.5 Å resolution[J]. Nature, 2001, 411(6840): 909−917.

[40] Zouni A, Witt H T, Kern J, et al. Crystal structure of photosystem II from *Synechococcus elongatus* at 3.8 Å resolution[J]. Nature, 2001, 409(6821): 739−743.

[41] Harrop S J, Wilk K E, Dinshaw R, et al. Single-residue insertion switches the quaternary structure and exciton states of cryptophyte light-harvesting proteins[J]. Proceedings of the National Academy of Sciences of the United States of America, 2014, 111(26): E2666−E2675.

[42] Ma Jianfei, You Xin, Sun Shan, et al. Structural basis of energy transfer in *Porphyridium purpureum* phycobilisome[J]. Nature, 2020, 579(7797): 146−151.

[43] Katoh T, Mimuro M, Takaichi S. Light-harvesting particles isolated from a brown alga, *Dictyota dichotoma*: a supramolecular assembly of fucoxanthin-chlorophyll-protein complexes[J]. Biochimica et Biophysica Acta (BBA)-Bioenergetics, 1989, 976(2/3): 233−240.

[44] Steinbeck J, Ross I L, Rothnagel R, et al. Structure of a PSI-LHCI-cyt b_6f supercomplex in *Chlamydomonas reinhardtii* promoting cyclic electron flow under anaerobic conditions[J]. Proceedings of the National Academy of Sciences of the United States of America, 2018, 115(41): 10517−10522.

[45] Sheng Xin, Watanabe A, Li Anjie, et al. Structural insight into light harvesting for photosystem II in green algae[J]. Nature Plants, 2019, 5(12): 1320−1330.

[46] Schmidt M, Krasselt A, Reuter W. Local protein flexibility as a prerequisite for reversible chromophore isomerization in α-phycoerythrocyanin[J]. Biochimica et Biophysica Acta (BBA)-Proteins and Proteomics, 2006, 1764(1): 55−62.

[47] Andrizhiyevskaya E G, Schwabe T M E, Germano M, et al. Spectroscopic properties of PSI–IsiA supercomplexes from the cyanobacterium *Synechococcus* PCC 7942[J]. Biochimica et Biophysica Acta (BBA)-Bioenergetics, 2002, 1556(2/3): 265−272.

[48] Burnap R L, Troyan T, Sherman L A. The highly abundant chlorophyll-protein complex of iron-deficient *Synechococcus* sp. PCC7942 (CP43′) is encoded by the isiA gene[J]. Plant Physiology, 1993, 103(3): 893−902.

[49] Ritter S, Hiller R G, Wrench P M, et al. Crystal structure of a phycourobilin-containing phycoerythrin at 1.90-Å resolution[J]. Journal of Structural Biology, 1999, 126(2): 86−97.

[50] Gantt E. Pigment protein complexes and the concept of the photosynthetic unit: chlorophyll complexes and phycobilisomes[J]. Photosynthesis Research, 1996, 48(1/2): 47−53.

[51] Wolfe G R, Cunningham F X, Durnfordt D, et al. Evidence for a common origin of chloroplasts with light-harvesting complexes of different pigmentation[J]. Nature, 1994, 367(6463): 566−568.

[52] Bishop N I. The β, ϵ-carotenoid, lutein, is specifically required for the formation of the oligomeric forms of the light harvesting complex in the green alga, *Scenedesmus obliquus*[J]. Journal of Photochemistry and Photobiology B: Biology, 1996, 36(3): 279−283.

[53] Fawley M W, Stewart K D, Mattox K R. The novel light-harvesting pigment-protein complex of *Mantoniella squamata* (Chlorophyta): phylogenetic implications[J]. Journal of Molecular Evolution, 1986, 23(2): 168−176.

[54] Harrison M A, Melis A. Organization and stability of polypeptides associated with the chlorophyll *a-b* light-harvesting complex of photosystem-II[J]. Plant and Cell Physiology, 1992, 33(5): 627−637.

[55] Bathke L, Rhiel E, Krumbein W E, et al. Biochemical and immunochemical investigations on the light-harvesting system of the cryptophyte rhodomonas sp. : evidence for a photosystem I specific antenna[J]. Plant Biology, 1999, 1(5): 516−523.

[56] Gundermann K, Schmidt M, Weisheit W, et al. Identification of several sub-populations in the pool of light harvesting proteins in the pennate diatom *Phaeodactylum tricornutum*[J]. Biochimica et Biophysica Acta (BBA)-Bioenergetics, 2013, 1827(3): 303−310.

[57] Eppard M, Rhiel E. The genes encoding light-harvesting subunits of *Cyclotella cryptica* (Bacillariophyceae) constitute a complex and heterogeneous family[J]. Molecular and General Genetics MGG, 1998, 260(4): 335−345.

[58] Caron L, Remy R, Berkaloff C. Polypeptide composition of light-harvesting complexes from some brown algae and diatoms[J]. FEBS Letters, 1988, 229(1): 11−15.

[59] Cock J M, Sterck L, Rouzé P, et al. The Ectocarpus genome and the independent evolution of multicellularity in brown algae[J]. Nature, 2010, 465(7298): 617−621.

[60] Durnford D G, Deane J A, Tan S, et al. A phylogenetic assessment of the eukaryotic light-harvesting antenna proteins, with implications for plastid evolution[J]. Journal of Molecular Evolution, 1999, 48(1): 59−68.

[61] Boldt L, Yellowlees D, Leggat W. Hyperdiversity of genes encoding integral light-harvesting proteins in the dinoflagellate *Symbiodinium* sp[J]. PLoS One, 2012, 7(10): e47456.

[62] Büchel C, Wilhelm C. Isolation and characterization of a photosystem I-associated antenna (LHC I) and a photosystem I—core complex from the chlorophyll c-containing alga *Pleurochloris meiringensis* (Xanthophyceae)[J]. Journal of Photochemistry and Photobiology B: Biology, 1993, 20(2/3): 87−93.

[63] Lichtlé C, Arsalane W, Duval J C, et al. Characterization of the light-harvesting complex of *Giraudyopsis stellifer* (chrysophyceae) and effects of light stress[J]. Journal of Phycology, 1995, 31(3): 380−387.

[64] Wiedemann I, Wilhelm C, Wild A. Isolation of chlorophyll-protein complexes and quantification of electron transport components in *Synura petersenii* and *Tribonema aequale*[J]. Photosynthesis Research, 1983, 4(1): 317−329.

[65] Simpson D J, Knoetzel J. Light-harvesting complexes of plants and algae: introduction, survey and nomenclature[M]//Ort D R, Yocum C F, Heichel I F. Oxygenic Photosynthesis: the Light Reactions. Dordrecht: Springer, 1996: 493−506.

[66] Jeffrey S W. Algal pigment systems[M]//Falkowski P G. Primary Productivity in the Sea. Boston, MA: Springer, 1980: 33−58.

[67] Schagerl M, Pichler C, Donabaum K. Patterns of major photosynthetic pigments in freshwater algae. 2. Dinophyta, Euglenophyta,

Chlorophyceae and Charales[J]. Annales de Limnologie-International Journal of Limnology, 2003, 39(1): 49−62.
[68] Wildman R B, Bowen C C. Phycobilisomes in blue-green algae[J]. Journal of Bacteriology, 1974, 117(2): 866−881.
[69] Zhang Yuzhong, Chen Xiulan, Zhou Baicheng, et al. A new model of phycobilisome in *Spirulina platensis*[J]. Science in China Series C: Life Sciences, 1999, 42(1): 74−79.
[70] Liu Luning, Aartsma T J, Thomas J C, et al. Watching the native supramolecular architecture of photosynthetic membrane in red algae: topography of phycobilisomes and their crowding, diverse distribution patterns[J]. The Journal of Biological Chemistry, 2008, 283(50): 34946−34953.
[71] Gardian Z, Tichý J, Vácha F. Structure of PSI, PSII and antennae complexes from yellow-green alga *Xanthonema debile*[J]. Photosynthesis Research, 2011, 108(1): 25.
[72] Kereïche S, Kouřil R, Oostergetel G T, et al. Association of chlorophyll a/c_2 complexes to photosystem I and photosystem II in the cryptophyte *Rhodomonas* CS24[J]. Biochimica et Biophysica Acta (BBA)-Bioenergetics, 2008, 1777(9): 1122−1128.
[73] Bai Xiaochen, McMullan G, Scheres S H W. How cryo-EM is revolutionizing structural biology[J]. Trends in Biochemical Sciences, 2015, 40(1): 49−57.
[74] Pi Xiong, Tian Lirong, Dai Huaien, et al. Unique organization of photosystem I-light-harvesting supercomplex revealed by cryo-EM from a red alga[J]. Proceedings of the National Academy of Sciences of the United States of America, 2018, 115(17): 4423−4428.
[75] Su Xiaodong, Ma Jun, Pan Xiaowei, et al. Antenna arrangement and energy transfer pathways of a green algal photosystem-I-LHCI supercomplex[J]. Nature Plants, 2019, 5(3): 273−281.
[76] Toporik H, Li Jin, Williams D, et al. The structure of the stress-induced photosystem I-IsiA antenna supercomplex[J]. Nature Structural & Molecular Biology, 2019, 26(6): 443−449.
[77] Shen Liangliang, Huang Zihui, Chang Shenghai, et al. Structure of a $C_2S_2M_2N_2$-type PSII-LHCII supercomplex from the green alga *Chlamydomonas reinhardtii*[J]. Proceedings of the National Academy of Sciences of the United States of America, 2019, 116(42): 21246−21255.
[78] Nagao R, Kato K, Suzuki T, et al. Structural basis for energy harvesting and dissipation in a diatom PSII-FCPII supercomplex[J]. Nature Plants, 2019, 5(8): 890−901.
[79] Pagliano C, Nield J, Marsano F, et al. Proteomic characterization and three-dimensional electron microscopy study of PSII-LHCII supercomplexes from higher plants[J]. Biochimica et Biophysica Acta (BBA)-Bioenergetics, 2014, 1837(9): 1454−1462.
[80] Bibby T S, Nield J, Barber J. Iron deficiency induces the formation of an antenna ring around trimeric photosystem I in cyanobacteria[J]. Nature, 2001, 412(6848): 743−745.
[81] Watanabe M, Semchonok D A, Webber-Birungi M T, et al. Attachment of phycobilisomes in an antenna-photosystem I supercomplex of cyanobacteria[J]. Proceedings of the National Academy of Sciences of the United States of America, 2014, 111(7): 2512−2517.
[82] Chang Leifu, Liu Xianwei, Li Yanbing, et al. Structural organization of an intact phycobilisome and its association with photosystem II[J]. Cell Research, 2015, 25(6): 726−737.
[83] Liu Haijun, Zhang Hao, Niedzwiedzki D M, et al. Phycobilisomes supply excitations to both photosystems in a megacomplex in cyanobacteria[J]. Science, 2013, 342(6162): 1104−1107.
[84] Qin Xiaochun, Pi Xiong, Wang Wenda, et al. Structure of a green algal photosystem I in complex with a large number of light-harvesting complex I subunits[J]. Nature Plants, 2019, 5(3): 263−272.
[85] Wei Xuepeng, Su Xiaodong, Cao Peng, et al. Structure of spinach photosystem II-LHCII supercomplex at 3.2 Å resolution[J]. Nature, 2016, 534(7605): 69−74.
[86] Su Xiaodong, Ma Jun, Wei Xuepeng, et al. Structure and assembly mechanism of plant $C_2S_2M_2$-type PSII-LHCII supercomplex[J]. Science, 2017, 357(6353): 815−820.
[87] Ikeda Y, Yamagishi A, Komura M, et al. Two types of fucoxanthin-chlorophyll-binding proteins I tightly bound to the photosystem I core complex in marine centric diatoms[J]. Biochimica et Biophysica Acta (BBA)-Bioenergetics, 2013, 1827(4): 529−539.
[88] Nagao R, Ueno Y, Akita F, et al. Biochemical characterization of photosystem I complexes having different subunit compositions of fucoxanthin chlorophyll *a/c*-binding proteins in the diatom *Chaetoceros gracilis*[J]. Photosynthesis Research, 2019, 140(2): 141−149.
[89] Pi Xiong, Zhao Songhao, Wang Wenda, et al. The pigment-protein network of a diatom photosystem II-light-harvesting antenna supercomplex[J]. Science, 2019, 365(6452): eaax4406.
[90] Zhao Fangqing, Qin Song. Evolutionary analysis of phycobiliproteins: implications for their structural and functional relationships[J]. Journal of molecular evolution, 2006, 63(3): 330−340.
[91] Zhang J M, Shiu Y J, Hayashi M, et al. Investigations of ultrafast exciton dynamics in allophycocyanin trimer[J]. The Journal of Physical Chemistry A, 2001, 105(39): 8878−8891.
[92] Fleming G R, Van Grondelle R. Femtosecond spectroscopy of photosynthetic light-harvesting systems[J]. Current Opinion in Structural Biology, 1997, 7(5): 738−748.
[93] Akimoto S, Yamazaki I, Murakami A, et al. Ultrafast excitation relaxation dynamics and energy transfer in the siphonaxanthin-containing green alga *Codium fragile*[J]. Chemical Physics Letters, 2004, 390(1/3): 45−49.
[94] Hashimoto H, Sugisaki M, Yoshizawa M. Ultrafast time-resolved vibrational spectroscopies of carotenoids in photosynthesis[J].

Biochimica et Biophysica Acta (BBA)-Bioenergetics, 2015, 1847(1): 69−78.
[95] Collini E, Wong C Y, Wilk K E, et al. Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature[J]. Nature, 2010, 463(7281): 644−647.
[96] Dean J C, Mirkovic T, Toa Z S D, et al. Vibronic enhancement of algae light harvesting[J]. Chem, 2016, 1(6): 858−872.
[97] Goss R, Lepetit B. Biodiversity of NPQ[J]. Journal of Plant Physiology, 2015, 172: 13−32.
[98] Pan Xiaowei, Ma Jun, Su Xiaodong, et al. Structure of the maize photosystem I supercomplex with light-harvesting complexes I and II[J]. Science, 2018, 360(6393): 1109−1113.
[99] Olaya-Castro A, Scholes G D. Energy transfer from Förster-Dexter theory to quantum coherent light-harvesting[J]. International Reviews in Physical Chemistry, 2011, 30(1): 49−77.
[100] 冷轩, 王专, 翁羽翔. 光合捕光天线系统的进化模式与能量传递[J]. 植物生理学报, 2016, 52(11): 1681−1691.
Leng Xuan, Wang Zhuan, Weng Yuxiang. Evolution of photosynthetic light harvesting antenna systems and energy transfer efficiency[J]. Plant Physiology Journal, 2016, 52(11): 1681−1691.
[101] Cao Jianshu, Cogdell R J, Coker D F, et al. Quantum biology revisited[J]. Science Advances, 2020, 6(14): eaaz4888.
[102] Ramanan C, Ferretti M, Van Roon H, et al. Evidence for coherent mixing of excited and charge-transfer states in the major plant light-harvesting antenna, LHCII[J]. Physical Chemistry Chemical Physics, 2017, 19(34): 22877−22886.
[103] Kirilovsky D. The photoactive orange carotenoid protein and photoprotection in cyanobacteria[M]//Hallenbeck P. Recent Advances in Phototrophic Prokaryotes. New York, NY: Springer, 2010: 139−159.
[104] McConnell M D, Koop R, Vasil'ev S, et al. Regulation of the distribution of chlorophyll and phycobilin-absorbed excitation energy in cyanobacteria: a structure-based model for the light state transition[J]. Plant Physiology, 2002, 130(3): 1201−1212.
[105] Adir N, Lerner N. The crystal structure of a novel unmethylated form of C-phycocyanin, a possible connector between cores and rods in pycobilisomes[J]. The Journal of Biological Chemistry, 2003, 278(28): 25926−25932.
[106] Lüder U H, Knoetzel J, Wiencke C. Two forms of phycobilisomes in the Antarctic red macroalga *Palmaria decipiens* (Palmariales, Florideophyceae)[J]. Physiologia Plantarum, 2001, 112(4): 572−581.

Algal light-harvesting system: Linkage of structures and functions by using structural biology

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Abstract: Algae are general term of a large group of photoautotrophic aquatic sporophytes. Along with the long earth history, the algal light-harvesting antenna has evolved special structure and function, to adapt to low-light underwater environment. Since the algal light-harvesting antennas were first discovered 70 years ago, the progress of structural analysis can be divided into four stages. The first stage was from 1950 to 1980, and effects were focused on studying the structural composition of light-harvesting antenna through biochemical and spectral techniques. The second stage was from 1980 to the present, and X-ray crystallization becomes a primary tool to study the partial fine-structure of the complete complex. The third stage was from 1980 to 2010. In this stage, complete contour structure can be studied by using electron microscope (EM). The fourth stage is from 2010 to the present, and the use of cryo-EM technology to studied intact fine-structure has brought the blowout period of structural analysis in recent year. With the rapid development of cryo-EM technology, a variety of complete fine-structures of algal light-harvesting antenna complexes have been analyzed, including cyanobacteria, red algae, green algae, and diatoms. Specifically, in 2019, multiple super-molecular complex structures of algal light-harvesting antenna were resolved. This breakthrough provides us valuable structure information for the study of energy transfer and the unified rela-

tionship between structure and function. However, the synthetic understanding of the relationship between the structure, function, environment, and applications of algal light-harvesting antennas is still preliminary, compared to the huge demand of solar energy utilization from bio-materials. Therefore, further research on the light adaptability of light-harvesting proteins has become the focus of the future, and will provide a sufficient scientific basis for the application of algal light-harvesting antenna proteins in the field of photoelectric devices.

Key words: algae; light-harvesting system; structural biology; structural analysis technology; efficient energy transfer; light adaption