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REVIEWS

# On the Edge of the Rainbow: Red-Shifted Chlorophylls and Far-Red Light Photoadaptation in Cyanobacteria

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**Abstract**—The phenomenon of photosynthetic adaptation of cyanobacteria to far-red light (FRL; 700–750 nm) is closely related to such basic themes as: phototrophy, microbial ecology, and diversity of bacteria. In applied terms, this bioenergetic strategy is essential for biotechnology, with a perspective to possess additional photosynthetic energy. The majority of cyanobacteria is known to use 400–700 nm light, excited state being channeled from light-harvesting complex to reaction centers of two photosystems containing chlorophyll (Chl) *a* showing red maxima at ~700 nm. After the isolation of first strains producing Chls *d* and *f* it became clear that cyanobacteria can also use FRL. Large amount of data has been obtained on cyanobacteria which constitutively produce Chl *d* as well as on those strains which produce Chl *f* or Chl *f*/Chl *d* during FRL photoacclimation (FaRLiP). Inclusion of these pigments in photosynthetic apparatus, particularly using FaRLiP mechanisms, augments the adaptive potential of cyanobacteria and expands their distribution range. The review provides evidence on such aspects as: photosynthetic apparatus containing Chl *d* or Chl*d*/Chl *f*; the FaRLiP gene cluster; phylogeny of cyanobacteria which constitutively or inducibly produce red-shifted chlorophylls; the use of chlorophylls in chemotaxonomy of cyanobacteria, and application of this character in nomenclature.

**Keywords:** far-red light, FaRLiP gene cluster, reaction center, light-harvesting complex, phycobilisome, photoadaptation, photosynthetic apparatus, chlorophyll *d*, chlorophyll *f*, cyanobacteria

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Light is a heterogenous energy source for phototrophy, in analogy to a multitude of substrates supporting chemotrophic metabolism. In this respect, pigment-protein complexes and chromoproteins which absorb differently energized quanta remind substrate specific enzymes. Not surprizingly, the terms "apoprotein" and "apoenzyme" are similar not only in sound, but also in their sense (here the Greek prefix apo- means *to undelie* that implies a protein moiety of photoreceptor and enzyme, correspondingly).

As in the case of various substrates, quanta in different parts of light scale are physiologically diverse. Thus, ultraviolet quanta ($\lambda$ < 400 nm) are relatively rich in energy although this energy is not assimilated rather it causes a damage (bleaching) of photosynthetic pigments. On the contrary, infra-red quanta ($\lambda$ > 750 nm) are relatively poor in energy; nevertheless, some anoxygenic bacteria can assimilate this energy. Light spectrum conditionally interpreted as a rainbow spanning from blue ($\lambda$ ~ 400 nm) to red ($\lambda$ ~ 700 nm) edge is used by cyanobacteria of Crown group and archaic class *Gloeobacteria* (Pinevich and Averina, 2021). Some cyanobacteria are even able to utilize far-red light (FRL; 700–750 nm). As the result, cyanobacteria inhabit all niches penetrated by 400–750 nm light using different mechanisms of photoadaptation.

The term "photoadaptation" refers to an ability to comply with the light regimes of different intensity (quantitative strategies) and spectral composition (qualitative strategies). The former strategies issue from an inverse relation between light intensity and the effective surface of light harvesting antenna: operationally, this state is achieved by changes in the total area of photosynthetic membranes as well as in size and package of photosynthetic units (Drews and Niederman, 2002). Qualitative strategies include: State 1 ↔ State 2 transition (Allen, 1992), complementary chromatic adaptation (Grossman et al., 1993), and photosynthetic adaptation to FRL (Averina et al., 2019).

Despite >700 nm quanta are relatively poor in energy, some bacteria produce FRL absorbing (red-shifted) metalloporphyrins—chlorophylls (Chls) and bacteriochlorophylls (BChls)—and modify photosynthetic apparatuses to such extent when the adaptation to FRL-rich niches becomes metabolically advantageous (Kühl et al., 2005).

Infra-red light is used by purple bacteria that produce BChl *a* or BChl *b* having absorbance maxima at

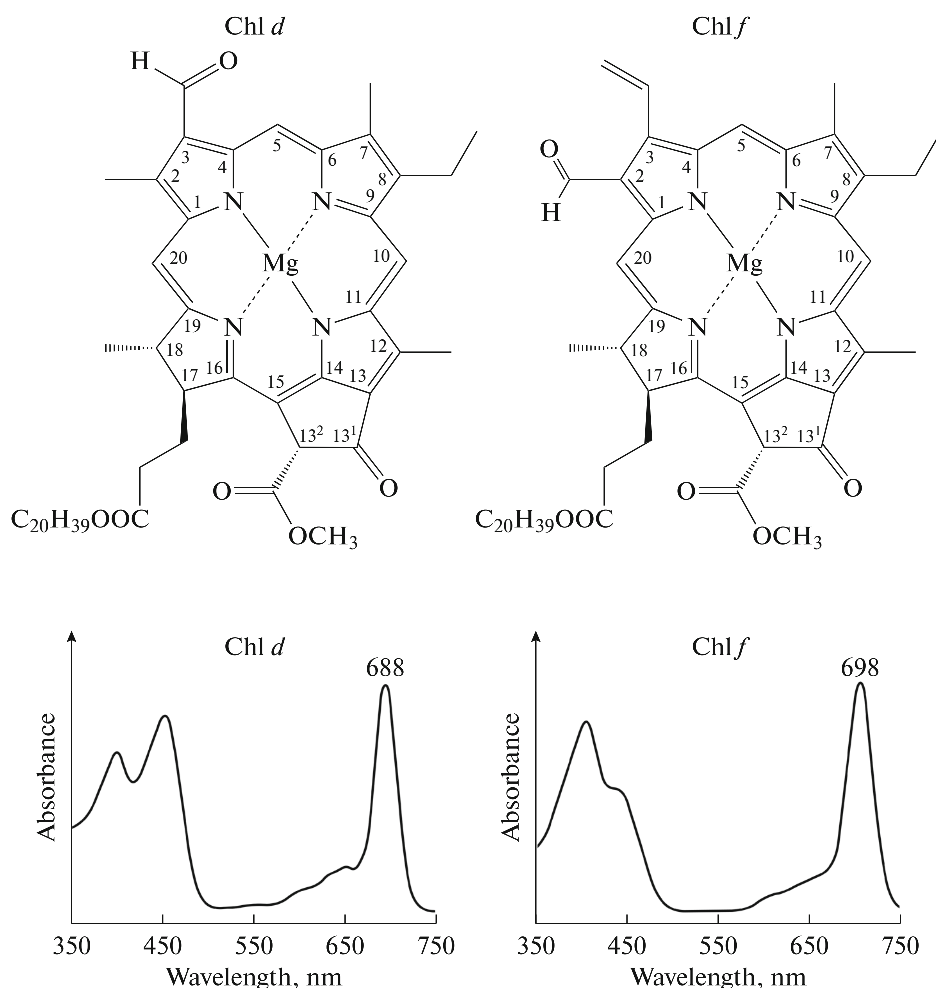


**Fig. 1.** Structural formulae of red-shifted chlorophylls (top row), and absorbance spectra in 100% acetone (bottom row; see: Averina et al., 2019).

800–900 and 980–1050 nm, correspondingly (Deisenhofer et al., 1985). Maxima of ≤800 nm are observed in BChl *g* of heliobacteria (Neerken and Amesz, 2001) as well as in BChls *c*, *d*, *e*, and *f* of green bacteria and chloracidobacteria (Amesz and Neerken, 2002; Bryant et al., 2007).

In the majority of cyanobacteria, light-harvesting complex (LHC) absorbs visible light, and excited state migrates to Chl *a* molecules in reaction centers (RCs) of photosystems (PSs) I and II with absorbance maxima at 700 and 680 nm, correspondingly. In cyanobacteria, photosynthetic adaptation to FRL could not be supposed until they were shown to produce red-shifted Chl *d* and Chl *f* (Miyashita et al., 1996; Chen et al., 2010). Very soon this type of bioenergetics has become a theme of many investigations, and the obtained results were compiled in review articles published nearly every year starting from 2010s (Loughlin et al., 2013; Gan and Bryant, 2015; Gan et al., 2015; Li and Chen, 2015; Allakhverdiev et al., 2016; Badshah et al., 2017; Averina et al., 2018, 2019; Sawicki and Chen, 2020; Friedrich and Schmitt, 2021). Our communication continues this series with an emphasis on recent contributions.

## RED-SHIFTED CHLOROPHYLLS

Chlorophylls, or magnesium chelates of esters formed by chlorophyllin acid with phytol and methanol, intensively absorb blue light (Soret band) and red light (Q-band, or $Q_y$-vector of energy transition). Red-shifted chlorophylls intensively absorb blue light and FRL (Fig. 1). Positions of absorbance maxima in situ or of chlorophyll-protein complexes differ from those in extracts of corresponding chlorophylls (French, 1960): in particular, red maximum is shifted to a larger wavelength. Chlorophylls are denoted in chronological order of their description by small Latin letters *a*–*f* except the letter *e* which has not been used because of unsupported discovery of "Chl *e*" in red algae; see: Larkum et al., 2018).

In functional terms, chlorophylls are classified into main and accessory: the former are incorporated in RCs while the latter is part of LHCs. The role of mediator between accessory and main chlorophylls is performed by small "core antennae" of RCs. These are autonomously ineffective: even in bright sunlight (e.g. during equatorial midday) the frequency of their transition to excited state would be less than the rate of electron transfer within RCs, hence a slow down of photosynthesis (Hunter et al., 1989). A bottleneck is surpassed due to the presence of LHCs—photosynthetic antennae with much larger effective cross-section (Blankenship and Chen, 2013).

Cyanobacteria typically produce only one chlorophyll—Chl *a*, which participates in reaction centers and core antennae; the role of LHC is performed by highly ordered aggregate of phycobiliproteins—phycobilisome (PBS) (Grossman et al., 1993). A small group of cyanobacteria termed "prochlorophytes" (Pinevich et al., 2010) employs, instead of PBS, the chlorophyll-protein complexes containing either Chl *a*/Chl *b* or Chl $a_2$/Chl $b_2$ (3,8-divinyl derivatives of respective chlorophylls). Cyanobacterial LHCs can also incorporate a minor Chl *c*-like pigment (Mg-3,8-divinyl protochlorophyllide, Mg-DVP) produced by some prochlorophytes as well as by Chl *d*-containing cyanobacterium *Acaryochloris marina* (Averina et al., 2019). Regarding red-shifted chlorophylls, Chl *d* is included not only in LHCs, but also in RCs whereas Chl *f* participates in LHCs and possibly in RCs.

The intensity of sunlight at Earth's surface is approximately the same in 600–700 and 700–800 nm range. But although large-wavelength quanta are poorer in energy than low-wavelength quanta, photosynthesis in >700 nm is less advantageous than in visible area, and thus cyanobacteria usually do not assimilate FRL. Nevertheless, some of them produce red-shifted Chl *d* and Chl *f*, and the zone of photosynthetically active radiation (PAR) spreads to large wavelengths of light spectrum (Kühl et al., 2005). However, a depth to which light penetrates water is inversely proportional to quantum's wavelength, and thus infra-red light is completely absorbed in few centimeters down from the surface. Additionally, in sea or in clear lake water the proportion of red light to FRL linearly increases with depth (Kirk, 1994), and FRL penetrates not deeper than 10 m (Gan et al., 2014). Therefore FRL-adapted cyanobacteria usually evade the upper foors of euphotic zone in seas and continental water bodies, but rather produce biofilms on (sub) littoral, soil, and stony substrates.

### *Chlorophyll d*

**Chemical structure and optical properties.** The C3-position in Chl *d* is occupied by a formyl group instead of vinyl in Chl *a* (Fig. 1). Correspondingly, Q-band is shifted to larger wavelength (665 → 688 nm, in 100% acetone; see Averina et al., 2019).

The discovery of Chl *d* is usually traced back to the study of pigments in Californian *Rhodophyceae* in early 1940s (Manning and Strain, 1943). As it was demonstrated later (Holt, 1961), originally published absorbance spectrum in fact belonged to 3-desvinyl-3-formyl Chl *a*, and this artifactual product could originate from technical inadequacy. In our times, the "mistery" concering Chl *d* discovery is alternately explained by presence of this pigment in cyanobacterial symbionts of red algae (Wood, 2012; Kiang et al., 2022). Anyway, authentic Chl *d* was firstly found in *A. marina* (Miyashita et al., 1996).

Chl *d* and its magnesium-free derivatives, pheophytin *d* and pyropheophytin *d*, have been found in sea sediments of Japan islands, on Bering Sea pelagial, in Antarctic salt lakes, and in freshwater lakes, e.g. the largest water pool of Japan, Lake Biwa (Kashiyama et al., 2008). Athough the aforementioned derivatives of Chl *d* can be obtained artificially in laboratories, the same abiotic reactions hardly happen in living nature, especially in the case of pyropheophytin; most likely these porphyrins are side products of Chl *d* and/or Chl *a* katabolism. At the same time, these data could be interpreted as an evidence of broad distribution of Chl *d*.

**Biosynthesis.** Different (bacterio)chlorophylls are produced at final stages of the global pathway (Bauer et al., 1993). Regarding Chl *d*, two scenarios are plausible: (1) direct transformation Chl *a* → Chl *d* because of a difference only in side radical; (2) the use of a separate branch in the global pathway (Loughlin et al., 2013). The first scenario is more likely (Fig. 2): in the experiments with *A. marina* grown in nutritional media supplied with $^{18}O_2$ or $H_2{}^{18}O$ formyl group contained an oxygen atom which originated from dioxygen rather than from molecule of water (Schliep et al., 2010). Since Chl *d* synthase has not been found, it was proposed that the oxydative reaction could be non-specifically catalized by P450-type cytochrome commonly participating in monoxydase reactions, or by special enzyme—pheophorbide *a* oxygenase (Chen and Blankenship, 2011; Yoneda et al., 2016). As it was shown in the experiments in vitro, Chl *d* was produced by an enzyme containing thiol group, e.g. cystein protease papain (Koizumi et al., 2005), or using low molecular thiocompounds (Fukusumi et al., 2012). That this transformation is associated with thiol-containing proteins or small molecules with HS-group was confirmed by transcriptome analysis of *Chlorogloeopsis fritschii* PCC 9212 wild type and mutants in the genes of regulatory proteins RfpA, RfpB, and RfpC (Ho and Bryant, 2019). In particular, Chl *d* priming PS II assembly could be produced using phycobiliprotein subunits rich in Cys-residues (Bryant et al., 2020).

**Fig. 2.** Schematic representation of terminal steps in the biosynthesis of red-shifted chlorophylls. Hypothetical reactions are indicated by dashed lines. Designations: Mg-DVP—Mg-3,8-divinyl protochlorophyllide; CaO—chlorophyll *a* oxygenase; CDS—chlorophyllide *d* synthase; CdS—chlorophyll *d* synthase; CFS—chlorophyllide *f* synthase; CfS—chlorophyll *f* synthase; GGR—geranylgeranyl reductase; GGDP—geranylgeranyl diphosphate; NADP(H)—oxidized and reduced nicotineamide adenine dinucleotide phosphate; $PP_i$—inorganic diphosphate (modified from: Averina et al., 2019).

### *Photosynthetic Apparatus in Cyanobacteria Constitutively Producing Chlorophyll d*

Cyanobacteria can produce red-shifted chlorophylls, and incorporate them in photosynthetic apparatus by two alternative strategies: constitutive synthesis of Chl *d,* and inducible synthesis of Chl *f* or Chl *f*/Chl *d*.

Chl *a* : Chl *d* ratio in *A. marina* (a mean value of 0.05) elevated at higher light intensity and lower oxygen partial pressure (Mimuro et al., 2004; Lin et al.,

2013). The processes of Chl *d* pheophytinization and dephytilation augmented in darkness and under anoxic conditions (Tsuzuki et al., 2022). Thus, the metabolism of Chl *d* is at least under dual environmental control.

Carotenoids were preferentially represented by zeaxanthin as well as α-carotene which substituted β-carotene typical for cyanobacteria (Miyashita et al., 1997).

The content of hydrophilic pigments is strain-specific. It was initially shown that *A. marina* MBIC 11017 contained phycocyanin (PC) and allophycocyanin (APC) (Hu et al., 1999), and that CpcA–G subunit genes were located on pREB3 plasmid while ApcA and ApcB encoding genes had a chromosomal location (Swingley et al., 2008). Later analyses of this strain showed that APC was present in trace amounts, and thus PC could function as a terminal energy transmitter (Bar-Zvi et al., 2018). Additionally, it was shown that ancestral PC genes were lost in evolution, and their distant homologues were acquired via horizontal transfer. In turn, *apcA* and *apcB* genes represent distant homologues of APC genes proper albeit their origin is unknown (Ulrich et al., 2021).

In contrast to MBIC 11017, the strains CCMEE5410 and HICR111A lacked PC and APC (Chen et al., 2009; Mohr et al., 2010; Miller et al., 2011).

**Light-harvesting complexes.** Chl *d* in *Acaryochloris* spp. has a dual role: as LHC chlorophyll, and as RC I and RC II chlorophyll (Itoh et al., 2007). The LHC common to PS I and PS II (Schiller et al., 1997; Chen et al., 2005c, 2005d) contains the proteins of CBP (Chlorophyll Binding Protein) superfamily. These 6-domain proteins can be employed for binding Chl *a*, Chl $a_2$, Chl *b*, Chl $b_2$ or Chl *d* (Chen et al., 2008; Pinevich et al., 2010). They are similar to the proteins of Cp43/IsiA family (CP43, or PsbC participates in RC II antenna; IsiA, or CP43' is PS II subunit induced by iron stress). Importantly, CBP proteins are dissimilar to 3-domain proteins of CAB (Chlorophyll *a*/*b*) superfamily present in chloroplasts (La Roche et al., 1996).

A group of 18 CBP proteins encircled three PS I complexes, and other 8 molecules flanked four PS II complexes (Chen et al., 2005a, 2005b). During iron stress, the CBP-A protein was substituted with the CBP-C protein; transcription of its gene was also induced by lower illumination (Chen et al., 2005a; Swingley et al., 2005).

As noted at the beginning of this section, the porphyrins of *A. marina* LHC can also include Mg-DVP. However, participation of this Chl *c*-like pigment in photophysical processes is questionable (Schliep et al., 2008); its role as key intermediate in the biosynthesis of chlorophylls seems more realistic (Fig. 2).

In addition to Chl *d*-containing LHC, *A. marina* has a phycobiliprotein-containing LHC (Chen et al., 2009). In contrast to hemidiscoid "standard PBS" (MacColl, 1998), this LHC represents a bundle of rods consisting from PC trimers (Niedzwiedzki et al., 2019). Because the "anchor" ApcB polypeptide is absent, it is not clear how such PBS attaches to the thylakoid; anyway, energy is effectively transmitted to RC II (Hu et al., 1999). PC trimers should be spectrally heterogeneous in order to promote unidirectional transfer of energy to the rod base. This condition is probably ensured by the synthesis of PC isoforms as well as using diverse linker polypeptides (Bar-Zvi et al., 2018; Niedzwiedzki et al., 2019). Anyway, by a parallel use of two LHCs *A. marina* gets an advantage over other FRL-adapted cyanobacteria (Loughlin et al., 2013).

**Reaction centers.** Heterodimeric PsaA/PsaB scaffold in *A. marina* RC I is 86% similar to type variant. Primary donor (P740) is represented by special pair—Chl *d*/CHl *d*' dimer (Chl *d*' is the $C13^2$-allomer of Chl *d*). Acccording to the consensus model (Fig. 3), primary donor interacts with primary acceptor (one of two Chl *a* molecules) and secondary acceptors as well as with Chl *d* in core antenna; redox potential of excited primary donor P740* equals −439 mV (Hu et al., 1998), i.e. nearly the same value as in primary donor P700* of RC I in most of cyanobacteria (Tomo et al., 2008). According to recent data, this model should be reconsidered. Thus, RC I is possibly of a unique type: primary acceptor ($A_0$) is pheophytin *a* instead of Chl *a*. Also, RC I is possibly trimeric; each monomer contains an additional Psa27 subunit, 70−77 Chl *d* molecules, one Chl *a* molecule, two pheophytin *d* molecules, 12−13 α-carotene molecules, two phylloquinone molecules, three Fe-S clusters, two phosphatidylglycerol molecules, and one monogalactosyldiglycerol molecule (Hamaguchi et al., 2021; Xu et al., 2021; Kimura et al., 2022).

RC II architecture has not been understood in detail. Concerning primary donor, there are two hypotheses. According to the first of them, primary donor is Chl *d* special pair (Itoh et al., 2007). A strong counter-argument is based on thermodynamic calculations (Allakhverdiev et al., 2016): energy absorbed by LHC would not drive a four-stroke mechanism of water oxidation (Cock's clock). After the second hypothesis, primary donor is Chl *a* special pair (P680) as commonly in cyanobacteria (Mimuro et al., 1999). However, in this case one has to admit that energy migrates against thermodynamic potential because LHC contains Chl *d* which is inferior to Chl *a* in the oscillation frequency of absorbed quanta. The second hypothesis was substantiated by 77 K fluorescence data (Mimuro et al., 1999, 2004) as well as by biochemical analysis showing that Chl *a* to pheophytin *a* ratio was 1 : 1 in different light regimes (Mimuro et al., 1999, 2000, 2004; Akiyama et al., 2002). Notably, both of these hypotheses were offered before the start of the experiments with *A. marina* membrane preparations.

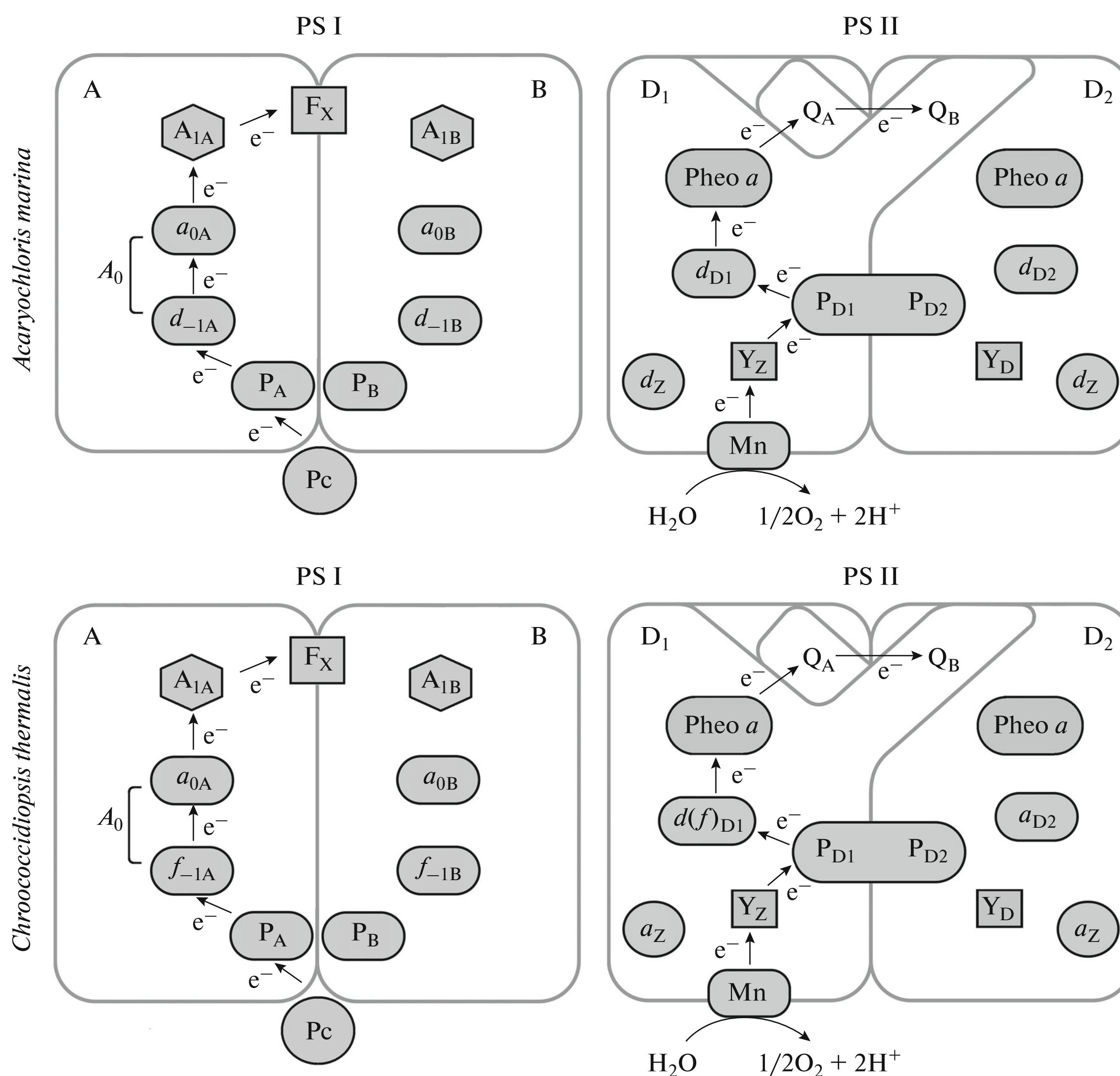


**Fig. 3.** Schematic representation of photosystems in cyanobacteria that produce red-shifted chlorophylls. See the text for details. Top left: PS I in *Acaryochloris marina*. Designations: A, B—scaffold heterodimer of subunits, correspondingly active and inactive branch; Pc—plastocyanin; $P_A$, $P_B$—primary donor (Chl *d* dimer); $A_0$ ($d_{-1A}$, $d_{-1B}$—Chl *d*; $a_{0A}$, $a_{0B}$—Chl *a*)—primary acceptor; $A_{1A}$, $A_{1B}$—intermediary acceptor; $F_X$— secondary acceptors (FeS-clusters). Bottom left: PS I in *Chroococcidiopsis thermalis*. Designations as above except $P_A$, $P_B$ (in this case, it is Chl *a* dimer) and $A_0$ (in this case, $d_{-1A}$ means Chl *f* instead of Chl *d*). Top right: PS II in *A. marina* (modified from: Averina et al., 2018). Designations: D1, D2—caffold heterodimer of subunits, correspondingly active and inactive branch, $P_{D1}$, $P_{D2}$—primary donor (Chl *a*/Chl *d* heterodimer); $d_{D1}$, $d_{D2}$—primary acceptor (Chl *d*); Pheo *a*—intermediary acceptor (pheophytin *a*); $Q_A$, $Q_B$—secondary acceptors (quinones); $d_Z$—Chl *d* of the reaction center antenna; $Y_Z$, $Y_D$—Tyr residues; Mn—manganese cluster of $H_2O$-oxidizing complex. Bottom right: PS II in *Ch. thermalis*. Designations as above except $P_{D1}$, $P_{D2}$ (in this case, it is Chl *a* dimer) and $d_{D1}$ (in this case, instead of Chl *d* it can be Chl *f*). $a_Z$—Chl *a* of the reaction center antenna.

Later results obtained using infra-red spectroscopy with Fourier transform (FTIR), pointed to P713—Chl *d* special pair (Tomo et al., 2007); the data for PS II preparations were in agreement with this possibility (Itoh et al., 2007). On the contrary, thermodynamic calculations suggested that primary donor was Chl *a*/Chl *d* heterodimer (Renger and Schlodder, 2008). At present, the consensus model (Allakhverdiev et al., 2016) predominates; according to it (Fig. 3) RC II contains two pheophytin *a* molecules and six chlorophyll molecules, at least four Chl *d* molecules among them. Primary acceptor is possibly Chl *d* ($d_{D1}$) located at the acive branch while quasi-symmetric Chl *d* ($d_{D2}$) is at the inactive branch. Two remaining Chl *d* ($d_z$) molecules belong to reaction center antenna. Secondary acceptor is most probably pheophytin *a*. To summarize, unambiguous conclusions regarding *Acaryochloris* spp. RC II would be discredited by

future data obtained using an expanded circle of model strains and advanced analytical methods.

## CHLOROPHYLL *f*

Chl *f* is a minor chlorophyll (~10% of Chl *a*) in unicellular cyanobacteria such as *Aphanocapsa* sp. KC1 (Miyashita et al., 2014), strain NSW (Behrendt et al., 2015), *Synechococcus* sp. PCC 7335 (Gan et al., 2015), and *Altericista variichlora* CALU 1173 (Averina et al., 2021). This pigment was also found in filamentous strains, for instance *Halomicronema hongdechloris* C2206 (Chen et al., 2012), *Chlorogloeopsis fritschii* PCC 6912 (Airs et al., 2014), *Leptolyngbya* sp. JSC-1 (Gan et al., 2014), *Chlorogloeopsis* sp. PCC 9212 (Gan et al., 2015), and *Ch. fritschii* CALU 759 (Averina et al., 2018).

**Chemical structure and optical properties.** Due to a small difference between Chl *f* and Chl *a* (2-formyl group instead of 2-methyl; Fig. 1) Q-band is significantly displaced towards larger wavelength (665 → 698 nm, in 100% acetone; see Averina et al., 2019). Thus, excitation energy of Chl *f* is lower than in other known chlorophylls (Chen et al., 2010).

**Biosynthesis.** Because Chl *f* is regionally more oxidized than Chl *a*, this pigment is suggested to come from alternate pathways (Fig. 2). In the one case, methyl group in Chl *a* molecule is oxidized; in the other case, the target is chlorophyllide *a* (Chen et al., 2010; Miyashita et al., 2014; Ho et al., 2016). In agreement with reverse genetics and heterologic expression data, Chl *f* synthase in all FRL-adapting cyanobacteria is encoded by the *psbA4* gene (Ho et al., 2016). This gene is a paralogue of the genes from *psbA* family (PS II genes). Despite the product of this gene, PsbA4 has no domain for binding the manganese cluster of water oxidizing complex, it contains ligands for Chl *a* as well as the conservative Tyr ($Y_z$)-residue (Gan et al., 2015). Albeit Chl *f* was produced in trace amounts even in white light, adaptive biosynthesis of this pigment depended on FRL, i.e. the PsbA4 protein was also a light dependent oxidoreductase (Ho et al., 2017b; Shen et al., 2019). In order to avoid a mess between Chl *f* synthase gene and its paralogue encoding the PsbA1 subunit of RC II (also termed D1), it was offered to rename the *psbA4* gene into *chlF*, and the PsbA4 protein into ChlF (Ho et al., 2016). The *chlF* gene possibly belongs to an ancestral type while other *psbA* genes most possibly descended from it by means of duplication and divergence (Murray, 2012; Cardona et al., 2015). In other words, Chl *f* is a more archaic trait than PS II (Ho et al., 2016).

### *Photosynthetic Apparatus in Cyanobacteria Inducibly Producing Red-Shifted Chlorophylls*

**The problem of energy coupling between red-shifted chlorophylls and Chl *a*.** Taking into account that PS I and PS II are equipped with their respective pools of antennal Chl *f* molecules (Itoh et al., 2015), red-shifted chlorophylls can potentially transmit energy to Chl *a*. However, energy migration between Chl *f* and Chl *a* molecule is questionable for theoretical reasons. In fact, Chl *a* usually obtains energy from the pigments which intensively absorb visible light (Chl *b*, carotenoids, and phycobiliproteins in the first instance) while Chl *f* not only weakly absorbs light in this spectral region, but also emits strong fluorescence. Moreover, Chl *f* should obey Stokes' law (excited state should migrate to a pigment with larger absorbance maximum).

Nevertheless, energy route Chl *f* → Chl *a* molecule is not an uphill transfer (i.e. against thermodynamic potential). Namely, the ability to comply with second law of thermodynamics is possibly due to the conjunction of specific factors: (a) long stay of Chl *f* in excited state; (b) low Boltzmann's statistics entropy for a system of Chl *f* molecules; (c) short distance between Chl *f* and Chl *a*; (d) specific binding of red-shifted chlorophylls to apoproteins (Niedzwiedzki et al., 2014; Itoh et al., 2015; Allakhverdiev et al., 2016; Larkum et al., 2018). The role of Chl *f* as energy donor was substantiated by *H. hongdechloris* spectrometry (Tomo et al., 2014; Akimoto et al., 2015) as well as by theoretical calculations using mathematic modeling methods (Schmitt et al., 2019).

**Light-harvesting complexes.** According to a priori reasoning, Chl *f* is preferentially an antennal pigment (Chen and Blankenship, 2011; Allakhverdiev et al., 2016; Nürnberg et al., 2018). However, there is no data on a presence of chlorophyll-containing LHC in cyanobacteria with inducible synthesis of Chl *f* or Chl *f*/Chl *d*. At the same time, PBS rearrangements occurring at FRL adaptation are sufficiently studied. Thus, the number of cylindrical supercomplexes in PBS core of *Leptolyngbya* sp. JSC-1 was shown to decrease from three to two (Gan et al., 2014). Due to a new chromophore composition, absorbance peak of PBS core was displaced for 40 nm to larger wavelength (it is usually at ~650 nm; Glazer and Bryant, 1975). In FRL-adapted *H. hongdechloris*, five-cylinder core was replaced with two-cylinder core consisting of APC subunits with absorbance maxima at 653 and 712 nm (Li et al., 2016). FRL-adapted *Synechococcus* sp. PCC 7335 had "standard PBS" (three-cylinder core; peripheral rods consisting of PC and APC), and "mini-PBS" (two-cylinder core composed of allophycocyanins ApcB2, ApcD2/D3/D5, ApcE2, and ApcF). Absorbance maximum of "mini-PBS" was at larger wavelength (711 nm instead of 650 nm), and low temperature fluorescence peak was at 730 nm (Ho et al., 2017a).

Wavelength shifts implemented by "standard PBS" as well as the acquisition of "mini-PBS" promote energy transfer from APC to Chl *f*. Additionaly, large APC-containing antennae accelerated the process of charge separation in RC II while in other types of pho-

tosystems charge separation became slower at a larger LHC size (Mascoli et al., 2022).

**Reaction centers.** It is not known yet whether Chl *f* can be involved in primary photochemistry (Allakhverdiev et al., 2016). Experimental data for *Chroococcidiopsis thermalis* grown in FRL theoretically admit that Chl *f* participated in charge separation within RC I and RC II (Nürnberg et al., 2018) (Fig. 3). Obviously, photochemical activity of Chl *f*/Chl *f* (or Chl *f*/Chl *d*) special pair should depend on whether redox potential of excited state was larger in absolute magnitude than in P700* and P680* (Nürnberg et al., 2018).

FRL-grown *Ch. thermalis* was shown to contain 7–8 Chl *f* molecules in PS I, most of which belonged to core antenna (Shen et al., 2019; Gisriel et al., 2020). In turn, FTIR (Fourier Transform Infrared Spectroscopy) analysis of *Fischerella thermalis* demonstrated that all red-shifted chlorophylls were only antennal pigments (Cherepanov et al., 2020). However, previous study of these cyanobacteria using the same method (Nürnberg et al., 2018; Hastings et al., 2019) indicated that although primary donor ($P_A$/$P_B$) was not formed by red-shifted chlorophylls, Chl *f* might be primary acceptor – $f_{-1A}$ and/or $f_{-1B}$ (Fig. 3).

PS II chlorophyll moiety in FRL-grown *Ch. thermalis* was represented by Chl *a* (up to 30 molecules), four Chl *f* molecules, and one Chl *d* molecule. Only one molecule of red-shifted chlorophyll was involved in electron transfer, and it possibly belonged to special pair (Nürnberg et al., 2018). According to more detailed data, this molecule occupied the D1-position (Nürnberg et al., 2018; Judd et al., 2020) rather than the $P_{D1}$-position as it was previously thought (see Gorka et al., 2021). An alternate member of special pair could be red-shifted chlorophyll in the $P_{D2}$-position (Fig. 3). In other words, PS II special pair was concluded—albeit not finally—to be Chl *a*/Chl *f* or Chl *a*/Chl *d* heterodimers (Judd et al., 2020). Recent cryoelectron microscopy-based modeling of PS II in FRL-adapted *Synechococcus* sp. PCC 7335 helped to idenify one Chl *d* molecule in the $P_{D1}$-position, and four Chl *f* molecules in core antenna (Gisriel et al., 2021). In agreement with phylogenetic reconstructions, ancestral FRL-adapted PS II contained one electron-transfering Chl *d* molecule in reaction center and two Chl *f*/three Chl *a* molecules in core antenna; however, specific evolutionary scenarios explaining the establishment of modern PS II may be different (Gisriel et al., 2022).

Due to incorporation of red-shifted chlorophylls in PS II core, FRL-adapted cyanobacteria more efficiently responded to spectral changes than *A. marina* (Mascoli et al., 2022).

## THE GENE CLUSTER OF FAR-RED LIGHT PHOTOACCLIMATION

The FaRLiP (Far-Red Light Photoacclimation) gene cluster is responsible for a set of structure-functional adaptations to the light regime in which FRL predominates over visible light (Gan et al., 2014, 2015; Gan and Bryant, 2015). In the course of photoacclimation, the synthesis of Chl *f* or Chl *f*/Chl *d* was induced, and PS I, PS II, and PBS were transformed (Gan et al., 2014; Gan and Bryant, 2015; Gan et al., 2015). According to proteome data, metabolic pattern was generally undisturbed despite a qualitative shift in light regime. The changes in protein content selectively affected photosynthetic apparatus: apoproteins of Chl *f*-containing photosystems were produced, and subunits of red-shifted PBS were synthesized instead of "standard PBS" subunits (Chen et al., 2019).

According to free access data, the FaRLiP cluster is present in as many as 20 cyanobacterial strains (Gan et al., 2014, 2015; Trampe and Kühl, 2016; Antonaru et al., 2020) including unicellular cyanobacteria *Ch. thermalis* PCC 7203 and *Synechococcus* sp. PCC 7335 as well as filamentous strains *Calothrix* sp. PCC 7507, *Chlorogloeopsis* sp. PCC 9212 and *F. thermalis* PCC 7521.

The FaRLiP cluster contains 21 genes. These are primarily *rfpA*, *rfpB*, and *rfpC* genes coding for the proteins of two-component phosphorelay system (Zhao et al., 2015). The product of *rfpA* gene—photoreceptor RfpA—belongs to "knotless" (without a sensory PAS-domain) phytochrome group. Signal is transduced by CheY-like protein RfpC, and response regulator is the RfpB protein which has two CheY-like domains flanking a DNA-binding domain. RfpB protein positively regulates FaRLiP genes (Zhao et al., 2015; Ho et al., 2017b). Mutants in *rfpA*, *rfpB*, and *rfpC* genes of *Ch. fritschii* PCC 9212, *Ch. thermalis* PCC 7203, and *Synechococcus* sp. PCC 7335 did not produce Chl *f* although Chl *d* was produced in white light and FRL (Zhao et al., 2015). Regulatory genes of the FaRLiP cluster are usually located at chromosome in the succession *rfpB*–*rfpA*–*rfpC* (Gan et al., 2015), except for the new species *A. variichlora* (Averina et al., 2021) and *Kovacikia minuta* (Shen et al., 2022) in which *rfpB* gene stands away from *rfpA* and *rfpC* genes (Fig. 4).

Among regulatory FaRLiP genes are *psaA2*/*B2*/*F2*/*I2*/*J2*/*L2* genes paralogues that code for PS I subunits, as well as *psbA3*/*A4*/*B2*/*C2*/*D2* genes paralogues encoding PS II subunits. These subunits can bind not only Chl *a*, but also two red-shifted chlorophylls (Gan and Bryant, 2015). According to proteome analysis of *Leptolyngbya* sp. JSC-1, the scaffold of RC II is formed by the products of paralogue genes—PsbA3 and PsbA4 (Gan et al., 2014). PsbA3 contains a complete set of ligands to bind the manganese cluster of water-oxidizing complex as well as other photochemically active PS II components

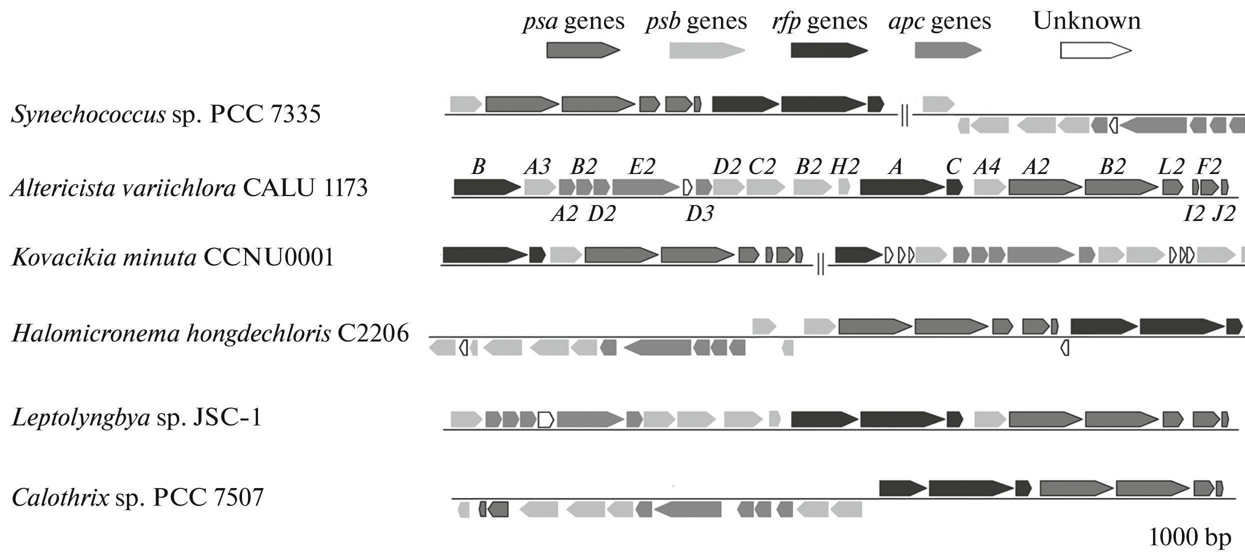


**Fig. 4.** Schematic representation of FaRLiP gene cluster present in cyanobacteria of different genera. Designations of genes from different groups are only shown for the previously described species *A. variichlora* (Averina et al., 2021).

(Murray, 2012; Cardona et al., 2015; Gan et al., 2015). At the same time, PsbA4 (also designated as srPsbA; *super rogue* PsbA, "especially distinct form of PsbA protein") was so modified that it even lacks a binding site for the manganese cluster (Murray, 2012; Cardona et al., 2015; Gan et al., 2015). As already noted, the PsbA4 protein also has an enzymatic activity as Chl *f* synthase: at heterologic expression of *Ch. fritschii* PCC 9212 and *F. thermalis* PCC 7521 *psbA4* genes in *Synechococcus* sp. PCC 7002, this strain produced Chl *f* (Ho et al., 2016; Shen et al., 2019). In other words, FRL-adapted photosystem with homodimeric PsbA4 or heterodimeric PsbA4/PsbA1 (D1) scaffold not only supplied electrons for photosynthetic electron transfer chain, but also catalyzed a biosynthetic reaction (Shen et al., 2019; Trinugroho et al., 2020).

The FaRLiP cluster additionally contains *apcA2/B2/D2/D3/E2* genes paralogues coding for allophycocyanin subunits in PBS core (Gan et al., 2014; Zhao et al., 2015). FRL adaptation also caused the synthesis of phycoerythrin and phycoerythrocyanin which are two phycobiliproteins with green (~550 nm) absorbance maxima (Gan et al., 2015; Soulier et al., 2020). In white light these pigments occupied the periphery of PBS rods, while in FRL the rods became shorter and were enriched with PC absorbing near-red light (~650 nm). Unlike allophycocyanin ApcA1 produced in white light, allophycocyanins ApcA2, ApcD2, and ApcD3 contained additional Cys-residues that could not bind chromophores and did not produce disulfide bridges (Gan et al., 2015; Herrera-Salgado et al., 2018; Bryant et al., 2020). Taking into account a decrease in Chl *d* content in FRL-adapted *Synechococcus* sp. PCC 7335 with mutant *apc* genes, additional Cys-residues were possibly involved in the synthesis of this chlorophyll (Bryant et al., 2020). The product of another paralogue gene, ApcE1 (also termed LCM; Linker Core-Membrane) binds PBS to thylakoid membrane; amino acid sequence of its N-terminus is similar to amino acid sequence of α-subunit in the ApcA1 allophycocyanin. Finally, although ApcE2 contains a chromophore-binding "pocket" (a.a. residues 180–230), phycocyanobilin is attached non-covalently, and absorbance maximum is displaced towards larger wavelengths (Gan et al., 2015; Miao et al., 2016; Ho et al., 2017a).

## CYANOBACTERIA CONSTITUTIVELY PRODUCING CHLOROPHYLL *d*

*A. marina* MBIC 11017, the first known Chl *d*-containing organisms, was isolated from a colony of the ascidian *Lissoclinum patella* in Western Pacific (Miyashita et al., 1996). In this case, red-shifted chlorophyll comprised the majority of chlorophyll molecules, while Chl *a* content was only 1–10% depending on light regime (Miyashita et al., 1997; Mimuro et al., 2004; Lin et al., 2013). Chl *d* producing strains were also isolated from symbiotic associations of *A. marina* with other ascidia—*Diplosoma* spp. (Kühl et al., 2005), *L. fragile* (López-Legentil et al., 2011), and *Cystodytes dellechiajei* (Martinez-Garcia et al., 2011). Together with the MBIC 110017 type strain, *A. marina*-related species were represented by epiphytic, epizoic, and endozoic strains from low altitude habitats of World Ocean: Awaji-1 (Murakami et al., 2004), CCMEE 5410 (Miller et al., 2005), MBIC 10697 (Swingley et al., 2005), HICR 111A (Mohr et al., 2010), MPGRS1 (Larkum et al., 2012), CRS (Behrendt et al., 2013), and Ssball 1 (Lin et al., 2013) as well as by epilithic and endolithic strains from different locations (see below).

### *Morphology and Ultrastructure in Cyanobacteria of the Genus Acaryochloris*

*Acaryochloris* spp. strains are organized in a separate cluster of dendrogram (Fig. 5). Their morphlogy is not too diverse: thus, in contrast to *A. marina* MBIC 11017 single cells (Miyashita et al., 1996), *Acaryochloris* sp. HICR111A cells produced irregular aggregates (Mohr et al., 2010). Lamellar system is also uniform: for instasnce, thin-sectioned thylakoids in *Acaryochloris* sp. CCMEE 5410 and MPGRS1 lay in parallell rows under cytoplasmic membrane (Miller et al., 2005; Larkum et al., 2012). In a special case of *Candidatus* Acaryochloris bahamensis, phycobiliprotein fluorescence zone at 640–670 nm did not supermipose onto Chl *d* fluorescence zone at ~750 nm (Lopez-Legentil et al., 2011). The observed anizotropy possibly reflected the uneven distribution of "mini-PBS" over lamellar system due to a vectorial orientation of symbionts within *L. fragile* body.

### *Ecogeographic Diversity of Acaryochloris* spp. *Strains*

These cyanobacteria inhabited marine and continental niches poor in white light. They produced biofilms and microbial mats (including stromatolites) and formed symbiotic associations with algae or invertebrates (Murakami et al., 2004; Kühl et al., 2005; Miller et al., 2005; Ohkubo et al., 2006; Mohr et al., 2010; Behrendt et al., 2011; Martinez-Garcia et al., 2011; Li et al., 2013).

**Inhabitants of coral reefs.** According to metagenome data, *Acaryochloris* spp. strains were often found in biofilms at coral reefs. The tags originating from such habitats, in particular *Acaryochloris* spp. 16S rDNA sequences comprised 5% of cyanobacterial sequences and 1.8% of total bacterial sequences (Behrendt et al., 2011). *Acaryochloris* spp. strains in particular HICR111A tendentiously colonized dead corals at Great Barrier Reef, as witnessed by morphological, spectroscopic, and molecular genetic data (Mohr et al., 2010; Behrendt et al., 2011, 2013).

**Symbionts of ascidians.** Most of Chl *d*-containing symbionts of ascidians were non-cultivable bacteria (Ohkubo and Miyashita, 2012). According to PCR data obtained with primers for the amplification of *Acaryochloris* 16S rDNA, symbionts of *Didemnum* spp., *Lissoclinum patella*, *L. punctatum*, and *L. timorense* were clustered in 14 phylotypes (Ohkubo and Miyashita, 2012). Chl *d*-containing symbionts of colonial ascidians *Diplosoma similis* and *D. virens* accumulated in the basal part of host body (Kühl et al., 2005). Cyanobacterial microcolonies with the same spectral characters as in *Acaryochloris* spp. attached themselves to the tunic of mediterranian ascidian *Cystodytes dellechiajei* (Martinez-Garcia et al., 2011). Chl *d*-containing strains multiplied not only within the tunic of adult *L. fragile* but also in larvae that could be due to a vertical inheritance of the microsymbiont. Taking into account <5% similarity of 16S rDNA with *A. marina* MBIC 11017, these cyanobacteria were ascribed to a candidate species *Candidatus* Acaryochloris bahamiensis (López-Legentil et al., 2011).

**Epiphytes.** Chl *d*-containing epiphytes were discovered in marine red algae *Ahnfeltiopsis flabelliformis*, *Callophyllis japonica*, and *Carpopeltis prolifera* using spectroscopy and fluorescence analysis (Murakami et al., 2004). According to 16S rDNA sequencing data, *A. marina* similar strains associated themselves with red algae *Caulacanthus ustulatus*, *Chondria crassicaulis*, *Ch. ocellatus*, *Gloiopeltis furcata*, and *Grateloupia lanceolata* as well as with green alga *Ulva pertusa* and brown alga *Undaria pinatifida* (Ohkubo et al., 2006). The strain MPGRS1 was isolated in Southeast Australia from red alga *Gelidium caulacantheum* which grew at a pneumatophore of *Avicennia marina* mangrove. A yellowish matter dispersed in water strongly absorbed visible light that promoted the growth of Chl *d*-producing cyanobacteria (Larkum et al., 2012). Subtropical forests of Central China were inhabited by a separate cyanobacterial ecotype: besides *Acaryochloris* sp. CCNUM4 it was represented by the strains closely related to some marine cyanobacteria (Zhang et al., 2019). Such strains associated themselves with mosses inhabiting calcareous rocks as well as with macrophytes in ponds and streams; all these niches were permanently shaded and, correspondingly, rich in FRL while the intensity of white light was only residual there. According to recent data, Chl *d* content in *Acaryochloris* spp. isolated on Californian littoral from red algae *Chondracanthus* sp. and *Neogastroclonium* sp. as well as from brown alga *Desmarestia* sp. comprised 99% of total chlorophyll (Kiang et al., 2022). Based on in situ spectrometry, this Chl *d* type had the absorbance maximum at shortest wavelength as compared to other red-shifted chlorophylls found in *Acaryochloris* spp. (Q-band at 704–705 nm).

**Epiliths and endoliths.** The strain CCMEE 5410 was isolated from a microbial mat at the floor of moderately halophilic Salt Lake, Southern California (Miller et al., 2005). Also, *Acaryochloris* spp. 16S rDNA tags were encountered in amplicon libraries obtained for the samples collected from rocky floors in water bodies of temperate and high altitudes. According to metagenome analysis, *Acaryochloris* spp.-similar strains were part of the microbial communities on Mayan pyramids (McNamara et al., 2006), Antarctic granite rocks (de los Rios et al., 2007), and fossil stromatolites of Bolivian Andes (Fleming and Prufert-Bebout, 2010).

Endoliths closely related to *Acaryochloris* spp. associated themselves with calcareous coralline algae. They were characterized by TaqMan-PCR in the material obtained from Red Sea and Great Barrier Reef, as well as in samples colleted on the sea shore in Spain and Kroatia; these cyanobacteria numbered

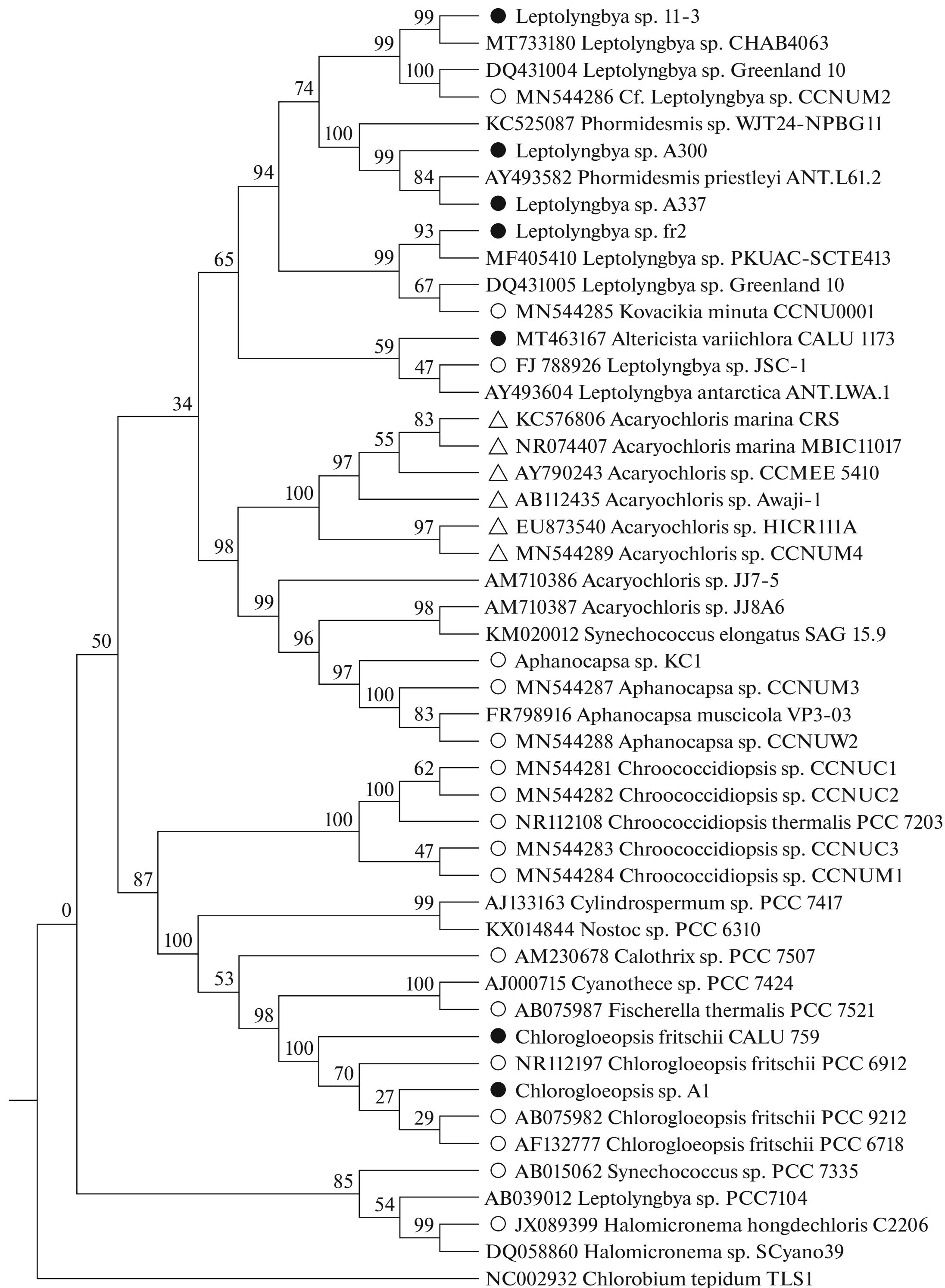


**Fig. 5.** Phylogenetic tree of cyanobacteria producing red-shifted chlorophylls, reconstrued by comparison of 16S rRNA gene sequences using the Maximum Likelihood method. At nodes—bootstraps for 1000 alternative trees; values of <50% are not shown. Designations: white triangles— strains that consitutively produce Chl *d*; white circles—strains that inducibly produce Chl *f* or Chl *f*/Chl *d*; black circles—strains that inducibly produce Chl *f*/Chl *d* (the authors' unpublished data except *A. variichlora* CALU 1173; see: Averina et al., 2021).

from 40 cells to $1.51 \times 10^3$ cells per mg sample (Behrendt et al., 2011, 2014).

## CYANOBACTERIA INDUCIBLY PRODUCING RED-SHIFTED CHLOROPHYLLS

As already noted, in contrast to *Acaryochloris* spp. permanently producing Chl *d*, some cyanobacteria can inducibly produce either only Chl *f* or Chl *f* in combination with Chl *d* (any strains with inducible synthesis of only Chl *d* have not been found).

These objects were isolated from seawater and freshwater lakes (Akutsu et al., 2011; Averina et al., 2018), thermal springs (Gan et al., 2014, 2015), bog soil (Airs et al., 2014; Gan et al., 2015), and carst caves (Behrendt et al., 2015). For the most part they produced biofilms and microbial mats including stromatolites (Chen et al., 2010; Trampe and Kühl, 2016).

### *Strains with Inducible Synthesis of Chlorophyll f*

Cultivable members of this group are few. The first of them, strain C2206 was isolated from a stromatolite in Shark Bay, Australia (Chen et al., 2010). The cells of this strain measuring 0.6–0.8 × 1.0–1.3 μm (close to a minimal size registered in cyanobacteria; see: Chisholm et al., 1992) produced non-branching trichomes enclosed in 100–200 nm wide sheath. Chl *f* was not produced in white light; in FRL-adapted cells it comprized 12.5% of Chl *a*. Using a polyphasic approach, this cyanobacterium was described as a new species *H. hongdechloris* (Chen et al., 2012).

*Aphanocapsa* sp. KC1 isolated from Lake Biwa (Akutsu et al., 2011) had 1.3–2.0 × 1.3–3.0 μm cells forming irregular aggregates; Chl *f* content was 8% of Chl *a* after two-week growth in FRL (Miyashita et al., 2014). Chl *f*-producing *A. muscicola* VP3-03 and 5N-04 as well as *Acaryochloris* sp. JJ8A6 and JJ7-5 were in a common cluster with Chl *d*-containing strains, although they did not synthesize the latter pigment (Miyashita et al., 2014). The strains similar to KC1 were isolated from biofilms in Jenolan carst caves, Australia (Behrendt et al., 2015).

Recent expeditions in wet subtropical forests of Central China have yielded Chl *f*-producing unicellular cyanobacteria of the genera *Aphanocapsa* and *Chroococcidiopsis* as well as filamentous strains belonging to two previously unknown genera of the family *Leptolyngbyaceae* (Zhang et al., 2019).

### *Strains with Inducible Synthesis of Chlorophylls f and d*

Such strains, in particular unicellular cyanobacteria *Chroococcidiopsis thermalis* PCC 7203 and *Synechococcus* sp. PCC 7335, were isolated from soil near Greifswald city, Germany, and from a mollusc shell collected on the littoral near Puerto-Peñasco city, Mexico (Gan et al., 2015). Filamentous cyanobacterium *Calothrix* sp. PCC 7507 was isolated from a sphagnum bog in vicinity of Kastanienbaum city, Switzerland (Gan et al., 2015). Two strains of filamentous cyanobacteria of the genus *Chlorogloeopsis*—*Ch. fritschii* PCC 6912 and *Chlorogloeopsis* sp. PCC 9212—were obtained from a rice field in Allakhabad city region, India, and from a thermal spring near Orense city, Spain (Airs et al., 2014; Gan et al., 2015), correspondingly. Another two filamentous strains, *Leptolyngbya* sp. JSC-1 and *F. thermalis* PCC 7521 were obtained from a floating microbial mat in termal spring at LaDuke Camping, and from thermal spring in Mammoth II carst cave, both in Yellowstone National Park, USA (Gan et al., 2014, 2015). The sixth filamentous strain, *Leptolyngbya* sp. $CCM_4$ was obtained from a stromatolite near Cuatrociénegas city, Mexico (Gómez-Lojero et al., 2018). Finally, resulting from the retrospective screening in St. Petersburg microbial collection, the strain CALU 1173 previously identified as *Synechocystis* sp. was shown to produce Chl *d* and Chl *f*; this strain was reattributed to a new species *A. variichlora* using a polyphasic approach (Averina et al., 2021).

## PHYLOGENY AND TAXONOMY OF CYANOBACTERIA PRODUCING RED-SHIFTED CHLOROPHYLLS

**Phylogenetic relationships.** The strains of *Acaryochloris* spp. formed a compact phylogenetic cluster (Fig. 5). For this reason, constitutive synthesis of Chl *d* was considered the late evolutionary acquisition (Li and Chen, 2015). However, 16S rDNA similarity of a certain cyanobacterium with *A. marina* MBIC 11017 did not guarantee an ability to produce Chl *d*. For instance, the strain RCC1774 did not produce Chl *d* although it contained Chl *b* that empowered to establish a new species *A. thomasi* using a polyphasic approach (Partensky et al., 2018). Likewise, oil-degrading cyanobacteria KUAC 3056 and KUAC 3106 isolated from Persian Gulf could not produce Chl *d* (Al-Bader et al., 2013); based on 16S rDNA similarity with *A. marina* MBIC 11017, these strains could be ascribed to a new species of the genus *Acaryochloris.*

Unlike a dense clustering of strains constitutively producing Chl *d* (Fig. 5), the strains which inducibly synthesize red-shifted chlorophylls were shown to be evolutionary distant from one another (Chen et al., 2012; Airs et al., 2014; Gan et al., 2014, 2015; Miyashita et al., 2014; Behrendt et al., 2015). Correspondingly, the latter strategy was considered more archaic, although frequently occurring horisontal transfer of the FaRLiP cluster should not be ruled out (Gan et al., 2015).

**Taxonomic implications.** Situations when chlorophyll type has been used as a taxonomic marker, especially when this character was reflected in nomenclature, are relatively rare. The presence of chlorophylls *b*

or $b_2$ was a key character in taxonomic diagnoses of cyanobacteria of the genera *Prochloron* (Lewin, 1976), *Prochlorothrix* (Burger-Wiersma et al., 1989), and *Prochlorococcus* (Chisholm et al., 1992). Repeating element "*-chloro-*" in these generic names initially pointed to the presence of Chl *b*; moreover, it implied the ancestry ("*Pro-*") for *Chlorophyceae* (see: Lewin, 1976) although this proposal was later dismissed (see: Pinevich et al., 2010).

A permanent synthesis of Chl *d* was typical for three species of the genus *Acaryochloris—A. marina* (Miyashita et al., 2003), *Candidatus* A. bahamiensis (Lopez-Legentil et al., 2011), and *A. thomasi* (recently described according to provisions of the Botanical Code; Partensky et al., 2018). The choice of this generic name is not good: not only all bacteria are "*Acaryo-*," but also very many bacteria produce chlorophylls ("*-chloris*").

Cyanobacteria that inducibly produced red-shifted chlorophylls were distributed among the operational Subsections I–V in *Bergey's Manual* according to general morphology although ignoring phylogenetic distinctions (see: Castenholz, 2015). Thus, *H. hongdechloris* belongs to Subsection III; the species epithet is literally translated as "with red chlorophyll" (Chinese *hong-de* means "of red color") although in fact FRL-absorbing Chl *f* was implied (Chen et al., 2012). Finally, the species epithet *variichlora* in cyanobacteria of the genus *Altericista* (Subsection I) reflected an ability to produce different ("*varii-*") chlorophylls ("*-chlora*"), namely Chl *a*, Chl *f*, and Chl *d* (Averina et al., 2021).

## CONCLUSIONS

Current advances in the study of red-shifted chlorophylls and photosynthetic adaptation to FRL are due to a joint use of up-to-date analytical methods (especially provided by bioinformatics) with traditional search for, and description of previously unknown objects. The obtained data contribute to better understanding the mechanisms of phototrophy, as well as taxonomic diversity, spatial distribution, and environmental ecology of photosynthetic bacteria. Resulting from basic data, a new source of energy for industrial photosynthesis can be anticipated. At the same time, there are some tasks for future research such as: (1) missing details of Chl *d* and Chl *f* biosynthesis; (2) incomplete data on reaction centers and ligh-harvesting complexes in cyanobacteria with red-shifted chlorophylls; (3) true knowledge on the distribution, evolutionary history, and variability of the FaRLiP gene cluster; (4) deeper insight in phylogeny of cyanobacteria with red-shifted chlorophylls. Growing interest in the phenomenon of photosynthetic adaptation of cyanobacteria to FRL promises a plethora of new discoveries and insights.

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## COMPLIANCE WITH ETHICAL STANDARDS

The authors declare no conflicts of interest. The article contains no data of research with animal objects.

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