**CSIRO** PUBLISHING

*Functional Plant Biology*, 2015, **42**, 493–501
http://dx.doi.org/10.1071/FP14350

**Goldacre Review**

# Novel chlorophylls and new directions in photosynthesis research

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*This review originates from the Peter Goldacre Award 2013 of the Australian Society of Plant Scientists that was received by the second author.*

**Abstract.** Chlorophyll *d* and chlorophyll *f* are red-shifted chlorophylls, because their $Q_y$ absorption bands are significantly red-shifted compared with chlorophyll *a*. The red-shifted chlorophylls broaden the light absorption region further into far red light. The presence of red-shifted chlorophylls in photosynthetic systems has opened up new possibilities of research on photosystem energetics and challenged the unique status of chlorophyll *a* in oxygenic photosynthesis. In this review, we report on the chemistry and function of red-shifted chlorophylls in photosynthesis and summarise the unique adaptations that have allowed the proliferation of chlorophyll *d*- and chlorophyll *f*-containing organisms in diverse ecological niches around the world.

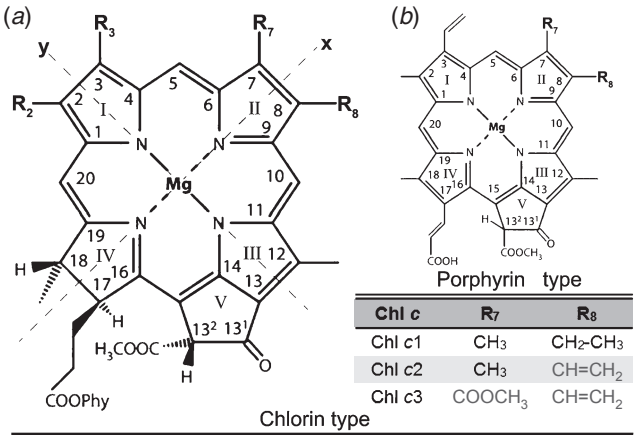
**Additional keywords:** *Acaryochloris*, chlorophyll *d*, chlorophyll *f*, cyanobacteria, *hongdechloris*, photosynthesis.

Received 12 December 2014, accepted 6 February 2015, published online 6 March 2015

## General distributions and properties of various chlorophylls

Chlorophyll (Chl) is derived from the Greek words meaning green (chloros) and leaf (phyllon) (Pelletier and Caventou 1818). They are greenish photopigments comprising a chlorin ring and a magnesium atom (Mg) with a long hydrophobic phytol chain attached (Fig. 1). Chlorophylls are only found in oxygenic photosynthetic organisms and they play a vital role in light-harvesting and energy transduction (Blankenship 2014). So far, five chlorophylls – named Chl *a*, *b*, *c*, *d* and *f* after the order of their discoveries – have been found in oxygenic photosynthetic organisms, including plants, algae and cyanobacteria (Chen *et al*. 2010; Chen 2014*a*, 2014*b*).

Chl *a* functions as a primary electron donor in nearly all oxygenic photosynthetic organisms (Björn *et al*. 2009), with a remarkable exception being found in the cyanobacterial group *Acaryochloris marina* (Miyashita *et al*. 1996). Chl *b* is found in the majority of eukaryotic photosynthetic organisms (virtually all plants and green algae), and it is considered to be the primary accessory pigment for light harvesting and energy transfer. Additionally, Chl *b* is present also in prochlorophytes, a group of cyanobacteria (La Roche *et al*. 1996). Chl *c* is a common name for more than three closely related pigments named Chl $c_1$, Chl $c_2$, and so on (Zapata *et al*. 2006). Structurally, they are quite different from other chlorophylls, and are porphyrins instead of chlorins (Fig. 1). They function as accessory photopigments in light-harvesting complexes and are universally present in many groups of marine algae, such as diatoms, brown algae and dinoflagellates (Zapata *et al*. 2006). Chl *d* was first discovered as a minor component in red algae pigment extractions 70 years ago (Manning and Strain 1943). Later, it was considered to be an artificial by-product created during the extraction process (Holt and Morley 1959; Holt 1961). The question of the presence of Chl *d* in photosynthetic organisms naturally was not resolved until the discovery of *A. marina* in 1996. Chl *d* is the predominant chlorophyll in this cyanobacterial species, constituting over 95% of total chlorophylls, depending on the culture conditions (Miyashita *et al*. 1996). Chl *d* can replace nearly all of the functions of Chl *a* in *A. marina*, not only in light-harvesting complexes (Chen *et al*. 2002; Tomo *et al*. 2011), but also in reaction centres (Hu *et al*. 1998; Chen *et al*. 2005; Tomo *et al*. 2007). So far, several strains of Chl *d*-containing organisms have been isolated and cultured, and all of those belong to one genus of cyanobacteria, *A. marina* (Miyashita *et al*. 1996; Murakami *et al*. 2004; Miller *et al*. 2005; Mohr *et al*. 2010; Larkum *et al*. 2012). There is very little information regarding Chl *e* due to only two cases being mentioned as, unpublished data around the 1940s (Chen *et al*. 2010). All referenced work regarding Chl *e* was HH Strain's, unpublished data in 1943 (pigment extraction from *Tribonema bombycinum*) and 1948 (pigment extraction from *Vaucheria hamata*) (Chen *et al*. 2010). Additionally, Chl *e* has never been isolated and chemically characterised, therefore, the existence of Chl *e* still needs to be proved. To avoid the subsequent confusion, the newly discovered chlorophyll as 'chlorophyll *f*' based on the order of chlorophylls reported. Chl *f* is the most red-shifted chlorophyll found to date (Chen *et al*. 2010). It was first discovered in a methanolic pigment extraction of stromatolites collected from Shark Bay, Hamelin Pool, Western Australia (Chen *et al*. 2010). Samples were cultured under infrared light (720 nm LED light) for the initial purpose




| Chl *c* | $R_7$ | $R_8$ |
|---|---|---|
| Chl *c*1 | $CH_3$ | $CH_2$-$CH_3$ |
| Chl *c*2 | $CH_3$ | CH=$CH_2$ |
| Chl *c*3 | $COOCH_3$ | CH=$CH_2$ |

| Chlorophylls | $R_2$ | $R_3$ | $R_7$ | $R_8$ | $Q_y$ |
|---|---|---|---|---|---|
| Chl *a* | $CH_3$ | CH=$CH_2$ | $CH_3$ | $CH_2$-$CH_3$ | 665.5 |
| 8-vinyl Chl *a* | $CH_3$ | CH=$CH_2$ | $CH_3$ | CH=$CH_2$ | 666.0 |
| Chl *b* | $CH_3$ | CH=$CH_2$ | CHO | $CH_2$-$CH_3$ | 652.0 |
| 8-vinyl Chl *b* | $CH_3$ | CH=$CH_2$ | CHO | CH=$CH_2$ | 658.0 |
| Chl *d* | $CH_3$ | CHO | $CH_3$ | $CH_2$-$CH_3$ | 697.0 |
| Chl *f* | CHO | CH=$CH_2$ | $CH_3$ | $CH_2$-$CH_3$ | 707.0 |

**Fig. 1.** Chemical structures of chlorophyll (Chl) with IUPAC/IUBMB numbering for carbon atoms, and the directions. (*a*) The structure of chlorin-type chlorophylls with different substitutions at rings I and II. (*b*) The structure of porphyrin-type chlorophylls (i.e. Chl *c* family) with different substitutions at ring II. Chlorin-type chlorophylls are esterified with the phytyl tail (Phy, $C_{20}H_{39}$), which is absent in Chl *c* family. The structure differences are highlighted in grey colour. $Q_y$ (nm) of Chl *a*, Chl *b*, Chl *d* and Chl *f* was recorded in 100% methanol (Li *et al*. 2012), and $Q_y$ (nm) of 8-vinyl Chl *a* and 8-vinyl Chl *b* was recorded in a mixture of methanol and acetone (Chen 2014*b*).

of isolating new Chl *d*-containing organisms. Further studies indicated that Chl *f* only occupied around 10% of the total chlorophylls in the marine filamentous cyanobacterium named *Halomicronema hongdechloris*, which was isolated and purified from the stromatolite sample as above. Further, Chl *f* is the first chlorophyll known in which its biosynthesis is directly induced by infrared light (Chen *et al*. 2012). More recently, Chl *f* was reported in other cyanobacteria (Akutsu *et al*. 2011; Airs *et al*. 2014; Gan *et al*. 2014; Miyashita *et al*. 2014).

## Spectral and photochemical properties of chlorophylls

The absorption spectra of chlorophylls can be described according to the 'four orbital' model (Gouterman 1961). Absorption spectra of chlorophyll show the electronic transitions along the *x*-axis of the chlorophyll running through the two nitrogen (N) atoms of rings II and IV, and along the *y*-axis through the N atoms of rings I and III (Fig. 1). The two main absorption bands in the blue and red regions are called Soret and Q bands, respectively, and these arise from π→π* transitions of four frontier orbitals (Weiss 1978; Petke *et al*. 1979; Hanson 1991). The lack of absorbance in the green spectral region, the so-called the 'green window', is responsible for the green colours of chlorophylls. The two lowest-energy transitions are called Q bands and the two highest-energy transitions are named B bands, also commonly called 'Soret bands' (Blankenship 2014). Taking Chl *a* as an example, the spectrum is characterised by two roughly separated Soret (B) bands at ~444 and 392 nm and a relatively strong $Q_y$ band near 667 nm in 100% methanol at 183 K (Li *et al*. 2013).

Structurally, Chls *b*, *d* and *f* are identical to Chl *a* with a chlorin macrocycle and a long phytol isoprenoid chain attached at $C_{17}$, except for the substitution of the (formyl group at different positions of the chlorin macrocycle (Fig. 1). Chl *f* and *b* share the same molecular formula ($C_{55}H_{70}N_4O_6Mg$), but the substitution of the formyl group is at the $C_2$ or $C_7$ position respectively (Fig. 1). Chl *d* ($C_{54}H_{68}N_4O_6Mg$) possesses a formyl group at the $C_3$ position, whereas a vinyl group is found in Chl *a* at this position (Fig. 1). These differences of macrocycle peripheral groups significantly affect the absorption spectra of the chlorophylls (Hoober *et al*. 2007). Compared with Chl *a*, the Soret band of Chl *b* is red-shifted to 457 nm compared with 435 nm of Chl *a* and its $Q_y$ band is blue-shifted to 646 nm in 100% acetone (Jeffrey and Humphrey 1975). The main Soret and $Q_y$ bands of Chl *d* are red-shifted to 470 and 700 nm in 100% methanol at 183K respectively (Li *et al*. 2013). The main Soret band of Chl *f* is blue-shifted to 408 nm and its $Q_y$ band is red-shifted to 712 nm in 100% methanol at 183K (Li *et al*. 2013), so that Chl *f* has the widest 'green window' among all known chlorophylls (Fig. 2) (Chen and Scheer 2013). Both Chl *d* and Chl *f* have the red-shifted $Q_y$ peaks compared with that of Chl *a*, therefore, Chl *d* and Chl *f* are also named as 'red-shifted' chlorophylls. Photosynthetic organisms containing red-shifted chlorophylls can thrive in environments where the infrared light is enriched and visible light is limited (Kühl *et al*. 2005), whereas the Chl *a*- photosynthesis is limited by available light due to its absorption properties (Fig. 2). In contrast, Chl *b*, a blue-shifted chlorophyll that extends the absorption of light towards the blue side of the 'green window', is more adapted to terrestrial light environments (Chen and Scheer 2013).

## Cyanobacterial strains possess unique chlorophylls

*Prochlorococcus* spp. are the smallest photosynthetic organisms known to date with the spherical diameter of 0.5 to 0.7 µm (Partensky *et al*. 1999). They use 8-vinyl Chl *a* and 8-vinyl Chl *b* (also named as 3,8, divinyl-Chl *a* and 3,8, divinyl-Chl *b*) instead of using the Chl *a* and Chl *b* (having monovinyl at $C_3$ position, Fig. 1) in their photosynthetic system (Goericke and Repeta 1992; Chisholm *et al*. 1992; Partensky *et al*. 1993, 1999). The Soret band of both 8-vinyl Chl *a* and 8-vinyl Chl *b* are red-shifted by 8–10 nm, compared with Chl *a* and Chl *b*, extending their absorbance at the blue side of the 'green window' (Morel *et al*. 1993; Moore *et al*. 1995; Partensky *et al*. 1999). The presence of 8-vinyl Chl *a* and 8-vinyl Chl *b* allows *Prochlorococcus* spp. to adapt to the ecological niches in the open-ocean, where blue light wavelengths are enriched (Partensky *et al*. 1999; Ito and Tanaka 2011).

*Acaryochloris marina* is a unicellular cyanobacterium that uses Chl *d* (constituting up to 90–99% of total chlorophylls) as its major photopigment to carry out oxygenic photosynthesis (Miyashita *et al*. 1996; Mimuro *et al*. 2004; Lin *et al*. 2013). *A. marina* strains are found widely through various ecological systems (Loughlin *et al*. 2013). Up to date, several strains of

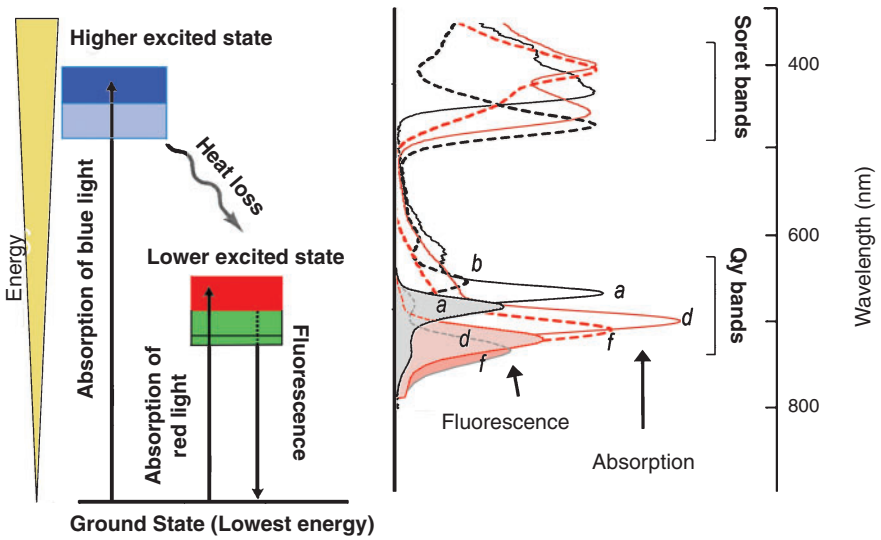



**Fig. 2.** The absorption and fluorescence spectra of chlorophylls (Chls) in 100% methanol and related energy level diagram. The blue and red boxes represent Chl *a* absorption region. The grey-blue represents the absorption extension at blue light region (mainly by Chl *b* and Chl *d*), and green boxes represent the absorption extension at red light region (mainly by Chl *d* and Chl *f*). The upward vertical arrows represent the vibronic transitions between the ground state and excited states. The Soret bands with shorter wavelength corresponds to a transition to a higher excited state. The $Q_y$ absorption band with longer wavelength of chlorophylls corresponds to light that has the energy required to cause the transition from the ground state to the first excited state. The downward vertical arrow indicates the fluorescence. Between absorption and florescence emission, relaxation processes as thermal equilibration occurs (heat loss). '*a*, *b*, *d* and *f*' represent Chl *a*, Chl *b*, Chl *d* and Chl *f* respectively.

*A. marina* have been isolated and cultured, *A. marina* MBIC11017 (Miyashita *et al*. 1996), *Acaryochloris* sp. AWAJI-1 (Murakami *et al*. 2004), *Acaryochloris* sp. CCMEE 5410 (Miller *et al*. 2005), *Acaryochloris* sp. HICR111A (Mohr *et al*. 2010), and *Acaryochloris* sp. MPGRS1 (Larkum *et al*. 2012). Chl *d*′ and Pheo *a* are present as minor components, but neither Chl *a*′ nor Pheo *d* is found in *A. marina* (Akiyama *et al*. 2001). *Acaryochloris* sp. MBIC 11017 has a unique phycobiliprotein arrangement, a rod-array structure rather than a typical phycobilisome (PBS) (Marquardt *et al*. 1997; Hu *et al*. 1998; Chen *et al*. 2009). Each rod consists of four discs that are formed by three hexamers ($\alpha_6\beta_6$). This structure is located at the stromal side of the thylakoid membrane and attached primarily to the PSII-antenna supercomplexes (Chen *et al*. 2009). Alpha-carotene and its derivatives are only found in two genera of cyanobacteria among all the prokaryotes: *Prochlorococcus* spp. and *Acaryochloris* spp. In *Acaryochloris*, α-carotene carries out the same function as β-carotene in the other cyanobacteria (Loughlin *et al*. 2013).

There are four different species of Chl *f*-containing cyanobacteria reported to date, *H. hongdechloris*, cyanobacterium strain KC1, *Leptolyngbya* sp. JSC-1 and *Chlorogloeopsis fritschii* PCC 6912 (Akutsu *et al*. 2011; Airs *et al*. 2014; Gan *et al*. 2014). *H. hongdechloris* belongs to the genus *Halomicronema* based on phylogenetic analysis and morphological features (Chen *et al*. 2012). It is reported that *H. hongdechloris* contains four main carotenoids and two chlorophylls, Chl *a* and *f* (Chen *et al*. 2012). Chl *a* is predominant chlorophyll under different light conditions (Chen *et al*. 2012; Li *et al*. 2014). Therefore, *H. hongdechloris* can acclimatise its pigment profiles to meet the requirements of the light environment: using Chl *f* to absorb infrared light under infrared-light-conditions and using phycobiliproteins and Chl *a* to absorb the visible light region of 400 to 700 nm. This infrared-light-inducible synthesis of Chl *f* appears to be the case for the other recent discoveries of Chl *f*-containing organisms: cyanobacterium strain KC1 (Akutsu *et al*. 2011), *Leptolyngbya* sp. JSC-1 (Gan *et al*. 2014) and *Chlorogloeopsis fritschii* PCC 6912 (Airs *et al*. 2014). Cyanobacterium strain KC1 is a unicellular cyanobacterium; it is closely related to unicellular cyanobacteria *Aphanocapsa muscicola* and has a sister relationship to clade of *Acaryochloris* spp. (Akutsu *et al*. 2011; Miyashita *et al*. 2014). The sequence of 16s rDNA between strains KC1 and *H. hongdechloris* only have 92% similarity (Miyashita *et al*. 2014). Similar to *H. hongdechloris*, the biosynthesis of Chl *f* only occurs when infrared light is present and Chl *a* always functions as major photopigment, under various light conditions. Therefore, it was suggested that Chl *f* may function not as primary donor in reaction centres, but instead as an antenna component where an uphill energy transfer would be required to deliver the excitation energy from Chl *f* to Chl *a* in reaction centres (Chen and Blankenship 2011).

*Leptolyngbya* sp. JSC-1 was isolated from a floating cyanobacterial mat from hot springs (~45°C) in the Yellowstone National Park, Montana, USA (Brown *et al*. 2010; Gan *et al*. 2014). Since *Leptolyngbya* sp. JSC-1 can thrive in hot environments up to 60°C; it is classified as a

thermotolerant cyanobacterium. *Leptolyngbya* sp. JSC-1 is filamentous with two morphotypes: isometric cells (length of 2.52 ± 0.41 μm, width of 2.16 ± 0.13 μm), and elongated cylindrical cells (length of 2.89 ± 0.27 μm, width of 1.62 ± 0.17 μm) (Brown *et al*. 2010). The cell sizes of cyanobacterium strain KC1 (unicellular cells with diameter of 1.3–2.0 μm and length of 1.3–3.0 μm) and *Leptolyngbya* sp. JSC-1 are much bigger than those of *H. hongdechloris* (length of 1.0–1.3 μm, width of 0.6–0.8 μm) (Chen *et al*. 2012; Miyashita *et al*. 2014). *Leptolyngbya* JSC-1 is a representative of a new genus of *Leptolyngbya* closed to *Leptolyngbya frigida* Ant. LH70.1 and *Leptolyngbya* sp. CENA 103 with <95% similarity (Fig. 3; Brown *et al*. 2010). It has been reported that strain *Leptolyngbya* sp. JSC-1 has a unique capability of synthesising nine carotenoids and three chlorophylls (Chl *a*, Chl *d* and Chl *f*) in response to different light conditions (Brown *et al*. 2010; Gan *et al*. 2014).

*Chlorogloeopsis fritschii* PCC 6912 (*C. fritschii*) was first isolated from the soils of paddy fields in India (Mitra 1950). *C. fritschii* has a diverse morphology and diversity of function depending on growth conditions (Evans *et al*. 1976), such as filaments and aseriate forms of irregular clumps of cells. Aseriate cells dominate under light condition of infrared light and natural light (Airs *et al*. 2014). *C. fritschii* is able to synthesise six carotenoids and three chlorophylls (Chl *a*, Chl *d* and Chl *f*) (Airs *et al*. 2014). We note that the production of Chl *f* and Chl *d* are found in *C. fritschii* grown under both infrared light and natural light conditions (Airs *et al*. 2014). The content of Chl *f* was maximised to ~6% of that total chlorophylls under infrared light condition (Airs *et al*. 2014), only half of that observed in *H. hongdechloris* grown under same condition. The highest ratio of Chl *d* to Chl *a* was maximum of 1% observed in infrared light-grown cells (Airs *et al*. 2014). Further, the ratio of Chl *f* to Chl *d* remained relatively unchanged when cells grown under both infrared light and nature light (Airs *et al*. 2014). In addition, the aseriate forms of *C. frischii* cells may create a microenvironment with enriched infrared light, due to the self-shading (Airs *et al*. 2014).

## Predicting the occurrence of Chl *f*-containing organisms and towards the isolation of novel Chl *f*-containing organisms

*H. hongdechloris* was isolated from the inner layers of stromatolites collected from Shark Bay, Western Australia (Chen *et al*. 2010, 2012). Since Chl *f* was discovered, only three other studies have reported the occurrence of Chl *f*-containing organisms. A comparison of the four organisms that have Chl *f* demonstrates that these organisms thrive in quite different ecological niches, including freshwater lakes, hot springs, the ocean and soil. These organisms also have very distinct morphological features. Two are filamentous and one is unicellular and all belong to different phylogenetic groups (Fig. 3). However, one common feature shared among them is the presence of Chl *f* when they are cultured under infrared light conditions. Thus, using >700 nm LEDs could play a significant role discovering the presence of Chl *f* and help improve our understanding of the ecological distribution of Chl *f*-containing organisms. This presents the possibility that Chl *f* production might be overlooked in many culture collections because infrared light not commonly applied in the culture of cyanobacteria or algae. The variation of Chl *f*-containing cyanobacteria also supports the idea that Chl *f* is the result of environmental adaptation.

Such organisms should only be found in certain habitats that are enriched in far-red light and depleted in visible light; for example, the interior of the microbial mat within the stromatolite where the first Chl *f*-containing organism was discovered (Chen *et al*. 2010, 2012). The visible region of light is absorbed by the photosynthetic organisms harboured in the upper layer. Cells residing beneath this layer are capable of utilising Chl *f* (or Chl *d*) in order to capture leftover infrared light to drive photosynthesis. However, knowledge of the distributions of Chl *f*-containing organisms in the environment is still largely unknown.

The acquisition of new or additional chlorophylls by photosynthetic organisms is thought to be an adaptation to the light quality of their niches (Croce and van Amerongen 2014). An organism that only contains Chl *a* (e.g. *Synechococcus*) cannot survive in an environment with 720 nm light (Duxbury *et al*. 2009), whereas *H. hongdechloris* thrives in infrared light (730 nm LED). Different $O_2$ evolution activities were observed between Chl *f*-containing infrared light-grown cells and white-light-grown cells, when illuminated by infrared light, which confirms the spectral expansion of oxygenic photosynthesis afforded by the presence of Chl *f* in *H. hongdechloris* (Li *et al*. 2014). These results not only demonstrate the benefit of possessing Chl *f* of extending the range of PAR to the infrared region, but also indicate that Chl *f* must contribute to the energy input of those cyanobacteria under such unique light conditions. Thus, the study of Chl *f* could improve our understanding of the ecological significance of spectral extension in natural photosynthetic systems (Chen and Blankenship 2011).

## Oxygenic photosynthesis and its physical limits

Photosynthesis is a biological solar energy storage process with two photo-excitation photosystem/reaction centres in oxygenic photosynthesis (Blankenship and Hartman 1998; Barber 2009; Kalyanasundaram and Graetzel 2010). The electron-donors P700 (PSI) and P680 (PSII), both Chl *a* molecules, will elevate the redox spans that allow the charge separation in the reaction centre and transfer the electron from water to NADP thermodynamically downhill (Fig. 4).

In general, oxygenic photosynthesis driven by Chl *a* and Chl *b* (not red-shifted chlorophylls) has long wavelength absorbance spectra extending to limits of ~700 nm due to the high energy requirements of splitting water and oxygen production (Björn *et al*. 2009). Removal of electrons from water requires powerful oxidative potential and hence the presence of P680 ($E_m$ = 1.23 V) is vital for oxygenic photosynthesis (Dau and Haumann 2008), although the long wavelength light has an excited state redox potential that is sufficiently negative to power the reduction of the primary electron acceptor, such as anoxygenic (non-oxygen evolving) photosynthesis driven by bacteriochlorophylls (Blankenship and Prince 1985).

Chl *a* was thought to be the only chlorophyll that can generate enough energy to split water and evolve oxygen as a by-product of oxygenic photosynthesis (Björn *et al*. 2009). It was thought

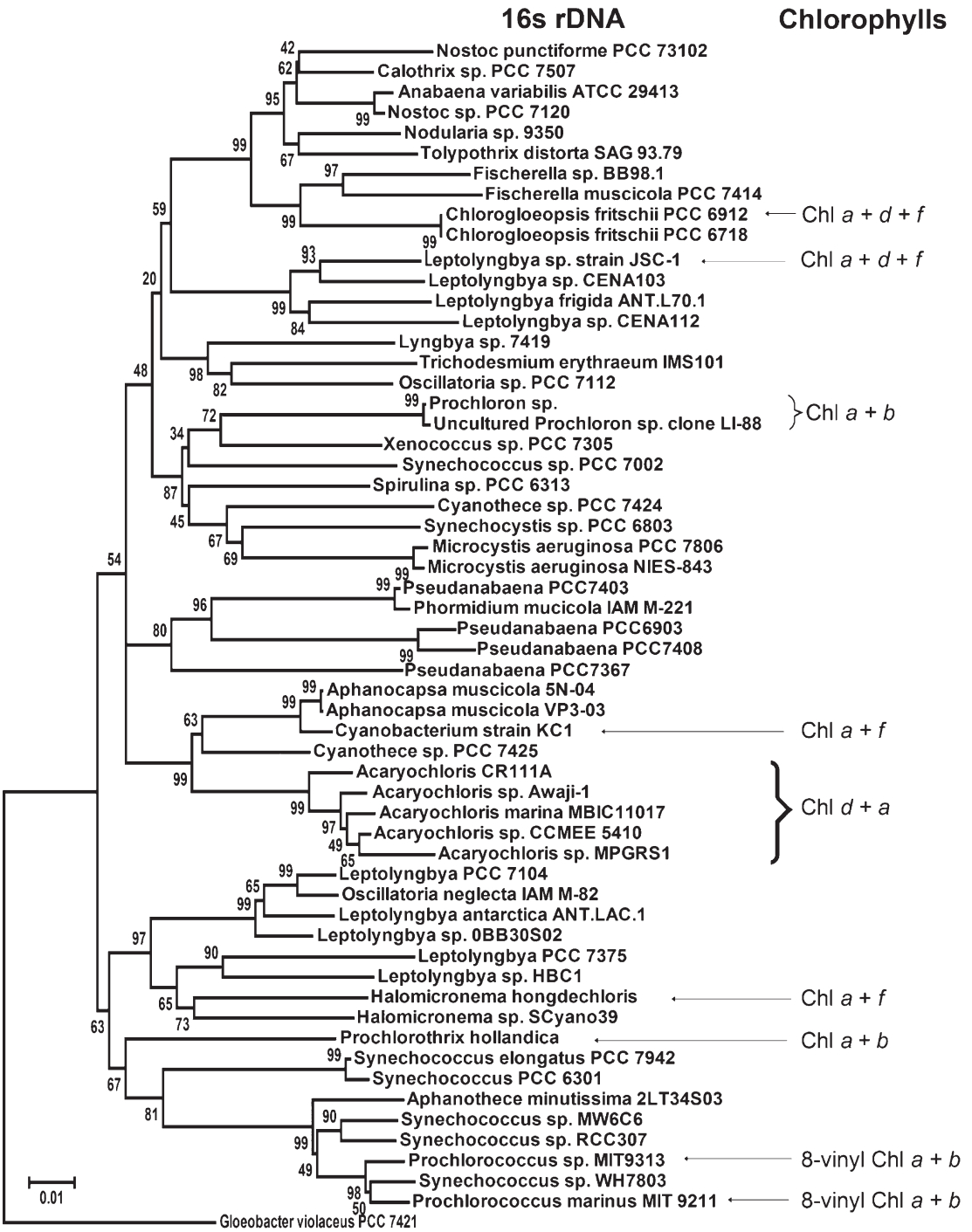



**Fig. 3.** Phylogenetic tree of cyanobacterial 16s rDNA. The unique chlorophyll contents are listed at right side. All others have chlorophyll *a* only. The phylogenetic tree was constructed by neighbour joining (NJ) method using 16S rDNA sequences of ~1025 bp (without gap). The sequences are aligned with multiple sequence alignment tools (Clustal W). The alignment was then manually edited based on the alignment of Chen *et al*. (2012). The evolution distance was calculated with Kimura 2-parameter model with 10 000 repeats using MEGA 5.0. The sequence data of *Acaryochloris* sp. Awaji-1, *Aphanocapsa muscicola* 5N-04, *Aphanocapsa muscicola* VP3–03, *Aphanothece minutissima* 2 LT34S03, *Calothrix* sp. PCC 7507, *Chlorogloeopsis fritschii* PCC 6718, *Chlorogloeopsis fritschii* PCC 6912, *Chlorogloeopsis* sp. PCC 9212, *Fischerella muscicola* PCC 7414, *Leptolyngbya frigida* ANT.L70.1, *Leptolyngbya* sp. CENA103, *Leptolyngbya* sp. CENA112, *Leptolyngbya sp*. strain JSC-1 are obtained from NCBI with accession number of AB112435, FR798920, FR798916, FM177488, NR102891, AF132777, NR112197, AB075982, AF132788, AY493574, EF088339, EF088337, FJ788926 respectively. The sequence data of Cyanobacterium strain KC1 is kindly provided by Professor Hideaki Miyashita. The other strains are downloaded from NCBI as described by Chen *et al*. (2012).

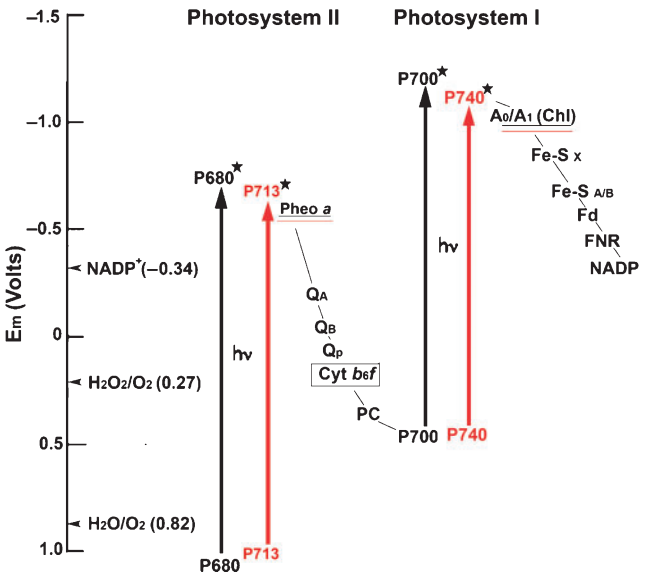



**Fig. 4.** Z-scheme of oxygenic photosynthesis and the comparison the energy levels of photosystems driven by chlorophyll *a* (P680 and P700) and chlorophyll *d* (P713 and P740). Black and red arrows represent the changes of redox potential generated by photoexcitation of the primary donors in the photosystems having different 'special pair' chlorophylls, blank arrows, chlorophyll *a*-photosystems; red arrows, chlorophyll *d*-photosystems. To explore the red-limits, the redox potential for water splitting ($H_2O/O_2$) or hydrogen peroxide ($H_2O_2/O_2$) and $NADP^+$/NADPH redox reactions are marked as references. The photosystem potentials are taken from Allakhverdiev *et al*. (2010).

that long wavelength light (>700 nm) contains low energy photons and is not sufficiently energetic to oxidise water (Blankenship and Prince 1985; Chen and Blankenship 2011). The traditional view of oxygenic photosynthesis was challenged with the discovery of red-shifted chlorophylls. Since 1996, research on Chl *d*-driven photosynthesis has expanded our understanding of the molecular mechanism of oxygenic photosynthesis (Loughlin *et al*. 2013). The investigation of Chl *d* and its photosynthetic reactions in *A. marina* has overturned the long-standing belief concerning the 'red-edge' of photosynthesis driven by Chl *a*.

The discovery of Chl *f* and its containing organisms open the PAR window even wider, predicting to extend the photosynthetic absorbance region up to 760 nm, far beyond the absorbance limits of 700 nm for Chl *a* and 740 nm for Chl *d*.

Previous studies have demonstrated that 'red chlorophylls' with $Q_y$ absorption maxima up to 760 nm can be found in several oxygenic photosynthetic organisms (Koehne *et al*. 1999; Schlodder *et al*. 2005; Wilhelm and Jakob 2006). These 'red chlorophylls' are mostly found in light-harvesting complexes, although the formation and function of those 'red chlorophylls' in energy storage is under debate (Melkozernov and Blankenship 2003; Corbet *et al*. 2007). The properties of these 'red chlorophylls' are accomplished using Chl *a*, whereby its spectrometric properties are modified by the protein environment, rather than modifying the chemical structure of the chlorophyll. However, the red-shifted spectrometric properties of Chl *d* and Chl *f* are accomplished by the modification of the chemical structure of the chlorophyll (Chen *et al*. 2010; Willows *et al*. 2013).

Chen and Blankenship (2011) suggested that an uphill energy transfer is needed to deliver excitation derived from red-shifted photons to the Chl *a*-containing reaction centres which had the normal absorbance spectra (P680 and P700) that are significantly 'bluer' (i.e. higher energy) than the red-shifted chlorophylls. In the Chl *d*-containing cyanobacterium, *A. marina*, Chl *d* (P740) replaces Chl *a* in P700, which prevents the energy transfer from a significant uphill energy transfer (Hu *et al*. 1998; Mimuro *et al*. 2000; Chen and Blankenship 2011). However, the red-shifted chlorophylls might encounter the energy losses during the subsequent photochemistry that critically affect the efficiency of electron-transfer, and thereby energy storage. A recent study investigating the redox potential of the Chl *d* special pairs in *A. marina* reported no differences for the redox potential level between Chl *a*-containing cyanobacteria and *A. marina* (Allakhverdiev *et al*. 2010; Allakhverdiev *et al*. 2011). For PSII reaction centre in *A. marina*, there is general agreement that Chl *a* is replaced by Chl *d*, at least at accessory sites ($Chl_{D1}$ and $Chl_{D2}$) (Chen *et al*. 2005; Tomo *et al*. 2007) and Pheo *a* (instead of Pheo *d*) is the primary acceptor of D1-side as in other oygenic photosynthetic organisms (Tomo *et al*. 2007, 2008). However, a controversy over the identities of the special pair chlorophylls in RC II has been debated more than 10 years due to the lack of the purified PSII reaction centre complexes (Chen *et al*. 2005; Itoh *et al*. 2007; Tomo *et al*. 2007). Further investigation is required for understanding the molecular mechanism of Chl *d*-photosynthesis, including the nature of RCII in *A. marina*. The energy transfer efficiency analysis of Chl *d*-photosynthesis revealed similar rates between Chl *a*-photosynthtic systems and Chl *d*-photosynthetic systems (Mielke *et al*. 2013).

Whether Chl *f* is involved in charge separation in the reaction centres, or only captures light energy in light harvesting complex, is still unknown. If Chl *f* is functional in light harvesting complexes, this means an uphill energy transfer is required for Chl *f* to deliver the energy to the Chl *a* in reaction centres. A new energy transfer pathway may be expected to support such a theory. However, if Chl *f* is involved in charge separation in the reaction centre, it is also unclear whether Chl *f* is capable of using the lower energy to oxidise water and produce oxygen. Water oxidation and oxygen production, driven by photosynthesis, requires higher energy input than non-oxygenic photosynthesis and it is this that determines the minimum energy input for photosynthetic reactions.

Chen and Blankenship (2011) point out the importance of the spectral region >700 nm. Due to the maximum solar spectrum occurring in spectral region >700 nm, and when the solar spectrum is represented as photon flux, every increment in the ability to utilise photons >700 nm can have a significant effect on the available energy utilised for photosynthesis. The ability to utilise light 50 nm outside the PAR spectrum (to 750 nm) results in an increase in the number photons available for photosynthesis by 19%. In oxygenic photosynthetic organisms, this expansion of the solar spectrum can be accomplished using available pigments such as red-shifted chlorophylls, especially the most red-shifted chlorophyll to date, Chl *f*. Such an expansion is recognised as a good potential source of photons to drive photosynthesis at higher efficiency.

The discovery of red-shifted chlorophylls has forced a re-evaluation of our understanding of the minimum threshold energy required for oxygenic photosynthesis. Studies of red-shifted chlorophylls have contributed to a better understanding of the molecular mechanisms of photosynthesis driven by red-shifted chlorophylls. The question remains as to whether or not this limit can be extended even further to longer wavelengths, and if so, how far the physical limit of oxygenic photosynthesis can hold. Understanding the mechanisms underlying the putative functions of Chl *f* in the reaction centres could help us to understand what the minimum threshold energy for oxygenic photosynthesis is. Chl *f* could possibly contribute to improving the efficiency of photosynthesis by extending the photosynthetically available spectrum further into the infrared than previously thought.

There are two potential applications of red-shifted chlorophylls. First, such chlorophylls would increase the ability of photosynthetic organisms to use light in an additional region of the solar spectrum. This could lead to significant improvements in agricultural efficiency or bioenergy storage if red-shifted chlorophylls can be integrated into algae or higher plants. This would theoretically give Chl *a*, *b* or *c*-containing oxygenic photosynthetic organisms access to approximately an additional 19% photon flux compared with other oxygenic photosynthetic organisms, which can only can absorb standard PAR (Chen and Blankenship 2011). An additional 19% photon flux in any oxygenic photosynthetic organism could be very significant on a global bioenergy scale. Such an increase could significantly increase food, fuel, or biomass production. Second, red-shifted chlorophylls may also be useful for remote sensing and detection of plants that contain this unique pigment due to their distinguishing red-shifted fluorescent properties.

## Acknowledgements

A special thank you to the Australian Society of Plant Scientists and Functional Plant Biology for their encouragement through the Goldacre award to MC (2013). MC also thanks the Australian Research Council for financial supports through the ARC Centre of Excellence for Translational Photosynthesis (CE1400015), Discovery Project (DP120100286) and ARC Future Fellow (FT120100464). YL thanks support from the China Scholarship Council.

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