

Perspective

Chlorophylls: A Personal Snapshot

Hugo Scheer

Bereich Systematik, Biodiversität und Evolution der Pflanzen, Universität München, Menzinger Str. 67, 80638 München, Germany; hugo.scheer@lmu.de

Abstract: Chlorophylls provide the basis for photosynthesis and thereby most life on Earth. Besides their involvement in primary charge separation in the reaction center, they serve as light-harvesting and light-sensing pigments, they also have additional functions, e.g., in inter-system electron transfer. Chlorophylls also have a wealth of applications in basic science, medicine, as colorants and, possibly, in optoelectronics. Considering that there has been more than 200 years of chlorophyll research, one would think that all has been said on these pigments. However, the opposite is true: ongoing research evidenced in this Special Issue brings together current work on chlorophylls and on their carotenoid counterparts. These introductory notes give a very brief and in part personal account of the history of chlorophyll research and applications, before concluding with a snapshot of this year's publications.

Keywords: chlorophylls; current research; applications; history

Chlorophyll (Chl) first came to me in a bottle containing approximately 1 kg of “Phäo-phytin Sandoz”, handed over by Hans-Herloff Inhoffen [1], the big boss of organic chemistry at the Technical University of Braunschweig. Herbert Wolf, one of the sous-chefs, had proposed using the Chl-macrocycle as a platform for studying the stereochemistry of side-chains for a diploma and later doctoral degree. The “Phäo-phytin Sandoz”, a mixture of (mainly) pheophytins *a* and *b* dating back from the time of Arthur Stoll [2] with Sandoz, proved an invaluable supply for making chemical modifications of the basic skeleton of chlorophyll *a*: after the first bottle ran out, it was replaced by another one and subsequently by a third one. Additionally, the spectroscopic tools available in Braunschweig, particularly circular dichroism and nuclear magnetic resonance, proved invaluable in analyzing the structure, including the stereochemistry, of the dozens of derivatives “cooked” from this material. As a postdoctoral researcher, I went to Joe Katz at Argonne National Laboratory. His group was famous for using the stable isotopes, ^2H and ^{13}C , for studying chlorophyll interactions in the test tube and in photosynthetic organisms [3]. I was lucky to have Jim Norris as a challenging guide. When we discussed his ideas of a “special pair” of Chls as the primary donor in photosynthesis, I remembered a selective deuteration from the Braunschweig lab that was key to proving the proposal by using Jim's advanced electron double resonance tools [4].

This time as an apprentice solidified my passion in Chls and subsequently to open-chain tetrapyrroles. It provided the basis for studying, over the next 45 years, several aspects of this group of molecules under many guises. They provide the basis for photosynthesis and thereby most life on Earth, in addition to several other functions. Besides their involvement in primary charge separation in the reaction center, they serve as light-harvesting and light-sensing pigments, they also have additional functions, e.g., in inter-system electron transfer. Chls also have a wealth of applications [5,6]: in basic science, modified pigments allow for functional analyses; in medicine, they serve as photosensitizers. Chl derivatives are used as colorants for food and cosmetics, they are also candidates for optoelectronic use. Much of the work performed in Braunschweig, Argonne, and later on in Munich refers to photosynthesis, although this was rather detached from living organisms. The extent of how detached it became is illustrated by two incidents. The first was when I handed



Citation: Scheer, H. Chlorophylls: A Personal Snapshot. *Molecules* **2022**, *27*, 1093. <https://doi.org/10.3390/molecules27031093>

Academic Editor: Eulogio J. Llorent-Martinez

Received: 27 December 2021

Accepted: 4 February 2022

Published: 7 February 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

my doctoral thesis to my parents. They were quite startled to see a such a tiny booklet of approximately 150 DIN A5 pages as the result of three years of work. Moreover, they confessed that they hardly understood anything besides the introductory sentences. The second incident was when my young children accompanied me one day to the basement at Argonne where all kinds of organisms were grown on stable isotope media. When I was shaving a plate of two-week-old wheat, their eyes lit up: for the first time, there was something familiar to them in the labs. Since then, I was a farmer of baby corn to them. It soon became obvious to them, however, that things really became interesting for me once the corn, the algae or the bacteria were crushed and their cells broken up.

It was satisfying to contribute during this time to the accumulated knowledge of tetrapyrroles, with the help of many students and technicians, in addition to funding from a variety of institutions of which the Deutsche Forschungsgemeinschaft was the most prominent one, in cooperation with groups from many countries of whom many become friends for life. The story of chlorophyll research goes back more than 200 years. The green extract of green plants and algae, then termed chlorophyll (Greek: green of leaves) by Pelletier and Caventou [7], later turned out to be a mixture of two non-fluorescent orange-yellow pigments and two blue tetrapyrrole pigments that fluoresce brightly [8]. While Stokes only gave incomplete details on how he came to this conclusion [9], it was verified by Fremy [10] and subsequently by Tswett [11], who coined the term chromatography for the novel separation developed with these pigments. The yellow pigments are carotenoids. The term chlorophyll has been narrowed to the family of tetrapyrrole pigments [12] which in plants are the blue Chl *a* and Chl *b*. The chemistry of these chlorophylls was studied early on by Willstätter's group [13] who realized their relation to heme. They also studied chlorophyllase and its hydrolyzing action on Chls. While it was one of the first enzymes to be isolated, its function *in vivo* remains enigmatic today [14]. The molecular structure of Chls *a* and *b* was solved by the group of Hans Fischer in 1942 [15]. Their stereochemistry was determined by Ian Fleming, by Burrell et al. and by Crabbé et al. (reviewed in Brockmann, [16]). Total syntheses were achieved by the groups of Strell [17] and, more rigorously, Woodward [18], but a general synthetic access of Chl-type pigments remains a challenge [19,20].

Chl-type pigments means that there are more than just Chls *a* and *b*. Stokes already mentioned a third chlorophyll present in brown algae, again without giving details [8]. Today, this is recognized as a mixture of several *c*-type chlorophylls [21]. Three more chlorophylls (Chls *d*, *e*, *f*) have been described in organisms capable of oxygenic photosynthesis [22–24], of which only the structures of Chl *d* [24,25] and Chl *f* [26] have been determined. They are supplemented by small amounts of especially tailored derivatives: the so-called prime pigments, isomers at C-13² of the parent compounds [27], the demethylated pheophytins, and pigments carrying alcohols different from the ubiquitous isoprenoid, phytol [27,28]. A much larger number of Chls, more precisely bacteriochlorophylls (BChls), has been found in photosynthetic bacteria [29]. Altogether, more than 100 (B)Chls are known in plants, algae and photosynthetic bacteria (Figure 1). A common feature of all is a long-lived excited singlet state, S₁, that in a monodisperse solution, results in bright fluorescence, while intersystem crossing to the phototoxic T₁ state is relatively low [30]. Their common structure is a cyclic tetrapyrrole with an additional isocyclic ring and, with only a single rare exception [31], a central metal Mg²⁺-ion. While the *c*-type Chls are true porphyrins, all others are chlorins reduced at ring D or bacteriochlorins reduced at rings B and D. These reductions result in an increased absorption and a red-shift of the redmost absorption band (Q_Y-band) that extends photosynthesis into the near-infrared spectral range down to 1050 nm.

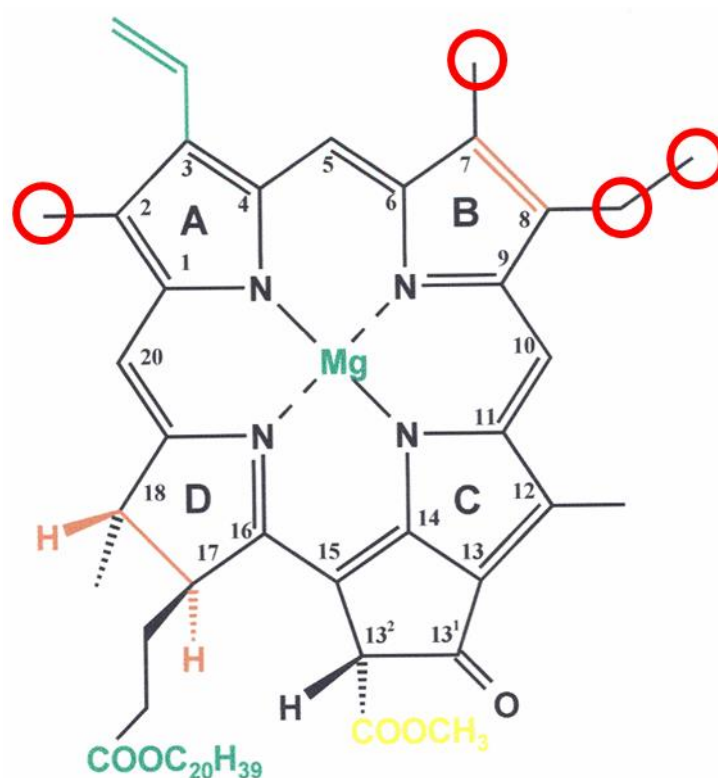


Figure 1. Structure of Chl *a*. Circles and colored bonds indicates modified sites in other Chls and BChls. Chl *b* and Chl *f* have a 7- and 1-CHO group, respectively. BChls *c*, *d* and *e* are characterized by lacking the 13²-COOCH₃, by a CHOH-CH₃-group at C2 (both stereoisomers), they differ by methylations at C20 and at the C8 and C12 substituents. In BChls *a*, *b* and *g*, the 7,8-double bond replaces the single bond, they differ in the substituents at C3,7 and/or 8. The c-type Chls are characterized by a 17,18-double bond, they differ by further modifications. Additional modifications in certain (B)Chls are replacements of the phytol esterifying the 17-propionic acid by other alcohols, mainly derived from farnesol or geranylgeraniol, exchange of the central Mg²⁺ by Zn²⁺ or inversion of the stereochemistry at C13². For further readings, see Ref. [24].

Regarding the long history of chlorophyll research [15,22,32–35], one would think that all has been said on these pigments. However, the opposite is true. Just by scanning through the publications of recent years, SciFinder lists 43,314 references since 2016. Additionally, while writing this preface, there have been publications, on an almost daily basis, on the various aspects of (B)Chls that witness unabated interest in these fascinating pigments and keep me reading on the various aspects of their structures, functions and uses. Moreover, ongoing research evidenced in this Special Issue brings together current work on Chls and on their carotenoid counterparts.

Let me illustrate this, before closing these notes, with a snapshot of publications from this year that refer to the various aspects of Chl research and applications. There is, firstly, the molecule itself. For better understanding the aromaticity of the parent chlorin and bacteriochlorin structures, their π -systems were compared to porpholactones, oxadervatives of chlorins and bacteriochlorins carrying a peripheral C=O group next to the oxa-O [36]. Compared to the fully unsaturated porphyrins, the ring-current in Chls and BChls bypasses the reduced peripheral positions. However, the π -density is partially restored in these formal single-bonds by the participation of non-bonding electrons of both oxygens. Another structural feature of most Chls is the isoprenoid alcohol esterified to the C17-substituent. The spectroscopic influence of the alcohol is distinct but minor [37], however, the alcohol is generally conserved among the different groups of photosynthetic organisms. In green plants, it is generally phytol. Increasing amounts of the precursor, geranylgeraniol, are found in *Arabidopsis thaliana* after growth in green light [38]. The

optical spectra of (B)Chls have been studied from the beginning. However, even these are open for surprises, as Leiger et al. [39] showed in their contribution to this Special Issue. They showed by anti-Stokes fluorescence that the red-most absorption band (Q_Y) has, at ambient temperature, has a tail extending far into the near-infrared. They ascribe it to the thermally activated vibronic coupling of the electronic transition. While the extreme red-shifts extending photosynthetic activity to lower energies can be ascribed in several cyanobacteria to chemically modified Chls *d* and *f* (see below), many organisms containing only Chl *a* show similar or even larger red-shifts; a prominent example is *Ostreobium* [40,41]. It is conceivable that the intensity of the band studied by Leiger et al. [39] is increased in these organisms by interactions with the protein. Chl cation radicals are formed in the primary reaction of photosynthesis by electron transfer. Orzel et al. [42] have now shown that in the presence of CuCl_2 , they can also be generated and participate in electron transfer in the dark.

Correlating function and spectroscopy to individual chlorophylls in native protein structures such as photosystem I remains a challenge. By polarized single-molecule spectroscopy, the individual Chls of the 96 present in the structure have been related to pigments absorbing at the blue and red edge of the spectrum [43]. In particular, the latter are relevant in localizing excitation energy near the reaction center. In this case, the red-shift is due to the still poorly understood interactions with the environment. In other cases, it relates to chemically modified pigments compared to the ubiquitous Chl *a*. Chls *d* and *f* carry peripheral formyl- instead of methyl-substituents at rings C and A, respectively (Figure 1) [24,44]. Such red-shifted Chls are relevant for cyanobacteria extending the hitherto-thought energetic limits of oxygenic photosynthesis [45]. In one such species, *Synechococcus thermalis* PCC 7335, their locations in photosystem I were identified by cryo electron microscopy: one Chl *d* is part of the primary donor and two Chl *f* are part of the core antenna [46]. A huge Bchl-complex largely devoid of protein is the chlorosome of green bacteria. Its structure is largely determined by BChl–BChl interactions between members of the BChl *c*, *d* and *e* family [47–49]. The group of Jürgen Köhler has used linear dichroism of single light-harvesting complexes from purple photosynthetic bacteria to obtain information on the pigment arrangement and its excitonic coupling [50]. In their contribution to this issue, Günther et al. [51] concluded that the powerful method reaches a limit with complexes of the size of the chlorosome of *Chlorobaculum tepidum*

The long lifetimes of excited singlet states (S_1) of Chls are crucial to their function in photosynthesis. They also pose problems to photosynthetic organisms, however, because they increase the chance for intersystem crossing to the triplet state (T_1) that subsequently generate singlet oxygen. Even though this process is minimized in the Mg-complexes [30], Chls are highly phototoxic under conditions of over-excitation of the photosynthetic apparatus when the productive use of the excitation energy is limited. A large fraction of the photosynthetic apparatus is therefore devoted to photoprotection [52], with carotenoids serving several lines of defense. The publication of Demming-Adams et al. in this Special Issue is devoted to a particularly effective carotenoid, zeaxanthin [42]. The role of carotenoids is, however, multi-faceted. As reviewed by Lokstein et al. in this issue [49], they often participate in light-harvesting, transferring their excitation with good to excellent quantum yields to Chls. Additionally, Makhneva et al. [53] presented an example from purple bacteria where the protective function against one ROS, e.g., singlet oxygen, seems negligible.

Phototoxicity also becomes relevant if (B)Chls are detached from their native protein complexes or during biosynthesis and biodegradation. The protection of phototrophic organisms during the metabolism of chlorophylls is ascertained by a variety of mechanisms. During biosynthesis, several control mechanisms have been recognized [54]: (i) the complete macrocyclic porphyrin system is only generated in the very last and tightly controlled step, all precursors are non-fluorescent and thereby non-phototoxic; (ii) the very late precursor is incorporated, in oxygenic organisms, in a light-activated reductase; (iii) once formed, Chls are bound to proteins which also contain carotenoids as protective pigments.

During biodegradation, the macrocycle is broken down after demetalation and dephytylation to non-phototoxic open-chain tetrapyrroles, the phyllobilins, on which all subsequent modification and degradation steps are performed [55]. Phototoxicity is also a potential problem in photosymbiotic partnerships, particularly for organisms harboring stolen and still active chloroplasts for several months (kleptoplasty) [56,57]. Last but not least, the phototoxicity of (B)Chls is a problem for herbivores including humans. Higher animals degrade Chl and its derivatives in their intestine [58] and have a low intestinal uptake [59]. This is combined with (at least) one excretory system; Szafraniec and Fiedor et al. [60] have now studied its specificity towards a variety of chlorophyll derivatives. Lower animals have developed a different strategy: they modify the structures by cyclization between the C-18 propionic side chain and C-13² of the isocyclic ring, thereby generating C-13¹ enols that are no longer phototoxic [61]. A massive reduction in excited-state lifetime has been known for peripheral metal complexes containing this structural element [62] and recently demonstrated as a characteristic feature of cyclo-enols [63].

The most widespread application of Chls are assays in plant biology. Often, the pigments are extracted and then spectrophotometrically analyzed [64,65]. Alternatively, the absorption or emission of (B)Chls is used for monitoring on time scales ranging from nanoseconds to years and spatial scales ranging from single molecules to the whole Earth or even outer space. Several reviews published in 2021 summarized current developments [66–72]. While these applications used the pigments as biological reporters, a current publication investigates the use of Chl *a* as an x-Ray dosimeter [73].

Moreover, there are much wider applications, probably the most advanced being their use as photosensitizers in medicine [74–77]. Their phototoxicity has generated interest in their use to tackle unwanted cells, from harmful microorganisms to tumors. Suvorov et al. reviewed the photodynamic therapy directed against microbes [74]. The capacity of porphyrins for generating singlet-oxygen has been used for almost 50 years in tumor therapy [75]. Phototoxicity is enhanced in chlorins and all the more in bacteriochlorins [78–80] due to increased absorption and a shift to longer wavelengths penetrating deeper into tissue. Moreover, when using Pd-derivatives of BChl, it became clear that additional reactive oxygen species are involved and indirect modes of attack are relevant. They are currently implemented in the treatment of pre-clinical prostate tumors [79]. Other medical applications are being developed in ophthalmology, a current example being cornea cross-linking [80]. Particularly elegant is their use in theranostics, in which phototoxic therapy is combined with diagnostic mapping, using either the same molecule for both purposes, or conjugates. A current publication on the latter uses a combination of a photosensitizing bacteriochlorin with naphthylimide fluorophores [81]. A general problem of using Chls in many such applications is their low stability and poor solubility. One of the solutions to overcome this is by solubilizing the pigments in detergent micelles. In their contribution to this issue, Janik-Zabrotowicz et al. [82] described the stabilization of Chl over extended times against light and oxygen by solubilizing it in polyoxyl 35 Castor oil (Chremophore EL) that forms exceptionally small micelles. It contains the pigment in monomeric form, thereby avoiding unwanted effects due to aggregation. Another common way is the introduction of polar side-chains that is facilitated by the functional peripheral substituents of (B)Chls. Again, only a current example shall be mentioned that uses polyethylene-glycol for this purpose [83].

The bright color of Chls in a range not covered by other natural dyes has led to many applications as colorants [6]. The additive E140 is regarded as chlorophyll, although it contains mainly oxidation products that retain the central Mg²⁺ ion and the lipophilic esterifying phytol (personal observation, unpublished). E140, E140i and E140ii have the central Mg²⁺ replaced by Cu²⁺, thereby reducing its phototoxicity. In recent work, Perezgalvez et al. [58] studied the composition of E140i, i.e., a lipophilic [Cu]–Chl preparation, and its degradation in the intestine. Last but not least, there is also work for stabilizing Chl (or at least derivatives retaining its color) for use in paints [84]. Vegetables and green algae are a source of a mixture of Chl *a* and Chl *b*. Cyanobacteria are a versatile source for pure

Chl *a* and its derivatives. Depending on the growth conditions [85], they also yield the blue, water-soluble phycocyanin carrying open-chain tetrapyrrole chromophores. In my group, we kept batches rich in Chl *a* and batches rich in phycocyanin as ready and easily stored supplies for these pigments for subsequent derivatization.

Much less developed are applications in the very realm of Chls, i.e., photovoltaics. While simple devices coined, e.g., synthetic leaf based on Chls are more than 50 years old, these pigments have thus far turned out too short-lived for applications, with the possible exception of chlorosome-like Chl aggregates [86]. The largest impact from natural photosynthesis is conceptual: the combination of reaction centers for charge separation with light-harvesting complexes that are adaptable to the quality and quantity of absorbed light is key to natural photosynthesis. Prototypes of photovoltaic devices applying this concept via dye-sensitized cells and, possibly, nano-particles relying on absorption enhancement by nanoparticles, reference some of the current reviews which conclude this personal snapshot [87–89].

Funding: The author thanks the University of Munich (*Ludwig-Maximilians-Universität*) and, in particular, the *department of systematics, biodiversity and evolution of plants*, for providing a workspace after retiring. The work received no current external funding. In the past, funding has been provided by many organizations, the most prominent being the Deutsche Forschungsgemeinschaft and the Alexander-von-Humboldt foundation.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: This work does not contain original data.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Quinkert, G. Hans Herloff Inhoffen in his times (1906–1992). *Eur. J. Org. Chem.* **2004**, *17*, 3727. [[CrossRef](#)]
2. Ruzicka, L. Arthur Stoll, 1887–1971. *Biogr. Mem. Fellows R. Soc.* **1972**, *18*, 567.
3. Katz, J.J.; Janson, T.R. Chlorophyll-Chlorophyll interactions from ¹H and ¹³C nuclear magnetic resonance spectroscopy. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 579. [[CrossRef](#)]
4. Norris, J.R.; Scheer, H.; Druyan, M.E.; Katz, J.J. An Electron-nuclear double resonance (ENDOR) study of the special pair model for photo-reactive chlorophyll in photosynthesis. *Proc. Natl. Acad. Sci. USA* **1974**, *71*, 4897–4900. [[CrossRef](#)]
5. Senge, M.O.; Richter, J. Adding color to green chemistry? An overview of the fundamentals and potential of chlorophylls. In *Biorefineries-Industrial Processes and Products: Status Quo and Future Directions*; Kamm, B., Gruber, P.R., Kamm, M., Eds.; Wiley-VCH: Hoboken, NJ, USA, 2005; p. 325. [[CrossRef](#)]
6. Humphrey, A.M. Chlorophyll as a color and functional ingredient. *J. Food Sci.* **2004**, *69*, C422. [[CrossRef](#)]
7. Pelletier, P.J.; Caventou, J.B. Sur la matière verte des feuilles. *Ann. Chim. Phys.* **1818**, *9*, 194–196.
8. Stokes, G.G. On the supposed Identity of Biliverdin with Chlorophyll, with remarks on the Constitution of Chlorophyll. *Proc. R. Soc.* **1864**, *13*, 144–145.
9. Stokes, G.G. On the application of the optical properties of bodies to the detection and discrimination of organic substances. *J. Chem. Soc.* **1864**, *17*, 304–318. [[CrossRef](#)]
10. Frey, E. Recherches chimiques sur la matière verte des feuilles. *Compt. Rend.* **1877**, *84*, 983–989.
11. Tswett, M. Adsorptionsanalyse und chromatographische Methode. Anwendung auf die Chemie des Chlorophylls. *Ber. Dt. Bot. Ges.* **1906**, *24*, 384–393.
12. Moss, G.P. IUPAC-IUB Joint commission biochemical nomenclature (JCBN). Nomenclature of Tetrapyrroles. Recommendation 1986. *Eur. J. Biochem.* **1988**, *178*, 277–328. [[CrossRef](#)] [[PubMed](#)]
13. Willstätter, R.; Hug, R. Isolierung des Chlorophylls. *Liebigs Ann. Chem.* **1911**, *380*, 177. [[CrossRef](#)]
14. Lin, Y.-P.; Charng, Y.-Y. Chlorophyll dephytylation in chlorophyll metabolism: A simple reaction catalyzed by various enzymes. *Plant Sci.* **2021**, *302*, 110682. [[CrossRef](#)] [[PubMed](#)]
15. Fischer, H.; Orth, H. *Die Chemie des Pyrrols*; Akademische Verlagsgesellschaft: Leipzig, Germany, 1940; reprinted, Johnson Reprint Corp: New York, NY, USA, 1968; Volume 2, 2nd half.
16. Brockmann, H., Jr. Stereochemistry and absolute configuration of chlorophylls and linear tetrapyrroles. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, NY, USA, 1978; Volume 2, pp. 288–321.
17. Strell, M.; Kalojanoff, A. Reactions in the chlorophyll series. VIII. *Synth. Pheophorbide Ann.* **1962**, *652*, 218–224.
18. Woodward, R.B.; Ayer, W.A.; Beaton, J.M.; Bickelhaupt, F.; Bonnett, R.; Buchschacher, P.; Closs, G.L.; Dutler, H.; Hannah, J.; Hauck, F.P.; et al. The total synthesis of Chlorophyll. *J. Am. Chem. Soc.* **1960**, *82*, 3800–3802. [[CrossRef](#)]

19. Liu, Y.; Zhang, S.; Lindsey, J.S. Total synthesis campaigns toward chlorophylls and related natural hydroporphyrins—Diverse macrocycles, unrealized opportunities. *Nat. Prod. Rep.* **2018**, *35*, 879–901. [[CrossRef](#)] [[PubMed](#)]
20. Chung, D.T.M.; Tran, P.V.; Chau Nguyen, K.; Wang, P.; Lindsey, J.S. Synthesis of model bacteriochlorophylls containing substituents of native rings A, C and E. *New J. Chem.* **2021**, *45*, 13302–13316. [[CrossRef](#)]
21. Zapata, M.; Garrido, J.L.; Jeffrey, S.W. Chlorophyll c pigments: Current status. In *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications*; Grimm, B., Porra, R., Rüdiger, W., Scheer, H., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp. 39–53.
22. Vernon, L.P.; Seely, G.R. *The Chlorophylls*; Academic Press: New York, NY, USA, 1966.
23. Majumder, E.L.-W.; Wolf, B.M.; Liu, H.; Berg, R.H.; Timlin, J.A.; Chen, M.; Blankenship, R.E. Subcellular pigment distribution is altered under far-red light acclimation in cyanobacteria that contain chlorophyll f. *Photosynth. Res.* **2017**, *134*, 183–192. [[CrossRef](#)]
24. Miyashita, H.; Ikemoto, H.; Kurano, N.; Adachi, K.; Chihara, M.; Miyachi, S. Chlorophyll d as a major pigment. *Nature* **1996**, *383*, 402. [[CrossRef](#)]
25. Holt, A.S.; Morley, H.V. A proposed structure for Chlorophyll d. *Can. J. Chem.* **1959**, *37*, 507–514. [[CrossRef](#)]
26. Willows, R.D.; Li, Y.; Scheer, H.; Chen, M. Structure of Chlorophyll f. *Org. Lett.* **2013**, *15*, 1588–1590. [[CrossRef](#)] [[PubMed](#)]
27. Kobayashi, M.; Akiyama, M.; Kise, H.; Watanabe, T. Unusual tetrapyrrole pigments of photosynthetic antennas and reaction centers: Specially tailored chlorophylls. In *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications*; Grimm, B., Porra, R., Rüdiger, W., Scheer, H., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp. 55–66.
28. Schoch, S. The esterification of Chlorophyllid a in greening bean leaves. *Z. Naturforsch.* **1978**, *33*, 712–714. [[CrossRef](#)]
29. Scheer, H. Overview. In *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications*; Grimm, B., Porra, R., Rüdiger, W., Scheer, H., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp. 1–26.
30. Kotkowiak, M.; Dudkowiak, A.; Fiedor, L. Intrinsic Photoprotective Mechanisms in Chlorophylls. *Angew. Chem. Int. Ed.* **2017**, *56*, 10457–10461. [[CrossRef](#)] [[PubMed](#)]
31. Wakao, N.; Yokoi, N.; Isoyama, N.; Hiraishi, A.; Shimada, K.; Kobayashi, M.; Kise, H.; Iwaki, M.; Itoh, S.; Kise, H.; et al. Discovery of natural photosynthesis using Zn-containing bacteriochlorophyll in an aerobic bacterium *Acidiphilium rubrum*. *Plant Cell Physiol.* **1996**, *37*, 889–893. [[CrossRef](#)]
32. Willstätter, R.; Stoll, A. *Untersuchungen über Chlorophyll*; Springer: Berlin/Heidelberg, Germany, 1913.
33. Scheer, H. (Ed.) *Chlorophylls*; CRC-Press: Boca Raton, FL, USA, 1991.
34. Grimm, B.; Porra, R.; Rüdiger, W.; Scheer, H. (Eds.) *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications*; Springer: Dordrecht, The Netherlands, 2006.
35. Golovko, T.K.; Gruszecki, W.I.; Prasad, M.N.V.; Strzalka, K. (Eds.) *Photosynthetic Pigments: Chemical Structure, Biological Function and Ecology*; Russian Academy of Sciences: Syktyvkar, Russia, 2014.
36. Guberman-Pfeffer, M.; Lalisce, R.; Hewage, N.; Brueckner, C.; Gascón, J. Origins of the Electronic Modulations of Bacterio- and Isobacteriodilactone Regioisomers. *J. Phys. Chem. A* **2019**, *123*, 7470–7485. [[CrossRef](#)]
37. Fiedor, L.; Kania, A.; Mysliwa-Kurziel, B.; Orzel, L.; Stochel, G. Understanding chlorophylls: Central magnesium ion and phytyl as structural determinants. *Biochim. Biophys. Acta* **2008**, *1777*, 1491–1500. [[CrossRef](#)]
38. Karlický, V.; Kmečová Materová, Z.; Kurasová, I.; Nezval, J.; Štroch, M.; Garab, G.; Špunda, V. Accumulation of geranylgeranylated chlorophylls in the pigment-protein complexes of *Arabidopsis thaliana* acclimated to green light: Effects on the organization of light-harvesting complex II and photosystem II functions. *Photosynth. Res.* **2021**, *149*, 233–252. [[CrossRef](#)]
39. Leiger, K.; Linnanto, J.M.; Freiberg, A. Establishment of the Qy Absorption Spectrum of Chlorophyll a Extending to Near-Infrared. *Molecules* **2020**, *25*, 3796. [[CrossRef](#)]
40. Wilhelm, C.; Jakob, T. Uphill energy transfer from long-wavelength absorbing chlorophylls to PS II in *Ostreobium* sp. is functional in carbon assimilation. *Photosynth. Res.* **2006**, *87*, 323–329. [[CrossRef](#)]
41. Koehne, B.; Elli, G.; Jennings, R.C.; Wilhelm, C.; Trissl, H. Spectroscopic and molecular characterization of a long wavelength absorbing antenna of *Ostreobium* sp. *Biochim. Biophys. Acta* **1999**, *1412*, 94–107. [[CrossRef](#)]
42. Orzel, L.; Rutkowska-Zbik, D.; van Eldik, R.; Fiedor, L.; Stochel, G. Chlorophyll a π -Cation Radical as Redox Mediator in Superoxide Dismutase (SOD) Mimetics. *ChemPhysChem* **2021**, *22*, 344–348. [[CrossRef](#)] [[PubMed](#)]
43. Hatazaki, S.; Sharma, D.; Hirata, S.; Nose, K.; Iyoda, T.; Kölsch, A.; Lokstein, H.; Vacha, M. Identification of Short- and Long-Wavelength Emitting Chlorophylls in Cyanobacterial Photosystem I by Plasmon-Enhanced Single-Particle Spectroscopy at Room Temperature. *J. Phys. Chem. Lett.* **2018**, *9*, 6669–6675. [[CrossRef](#)] [[PubMed](#)]
44. Chen, M.; Schliep, M.; Willows, R.D.; Cai, Z.-L.; Neilan, B.A.; Scheer, H. A Red-Shifted Chlorophyll. *Science* **2010**, *329*, 1318–1319. [[CrossRef](#)] [[PubMed](#)]
45. Psencik, J.; Mancal, T. Light harvesting in green bacteria. In *Light Harvesting in Photosynthesis*; Croce, R., van Grondelle, R., van Amerongen, H., van Stokkum, I.H.M., Eds.; Taylor & Francis—CRC Press: Boca Raton, FL, USA, 2018; pp. 121–155.
46. Tros, M.; Mascoli, V.; Shen, G.; Ho, M.-Y.; Bersanini, L.; Gisriel, C.J.; Bryant, D.A.; Croce, R. Breaking the Red Limit: Efficient Trapping of Long-Wavelength Excitations in Chlorophyll-f-Containing Photosystem I. *Chem* **2021**, *7*, 155–173. [[CrossRef](#)]
47. Gisriel, C.; Shen, G.; Ho, M.-Y.; Kurashov, V.; Flesher, D.; Wang, J.; Armstrong, W.; Golbeck, J.; Gunner, M.; Vinyard, D.; et al. Structure of a monomeric photosystem II core complex from a cyanobacterium acclimated to far-red light reveals the functions of chlorophylls d and f. *J. Biol. Chem.* **2021**, 101424. [[CrossRef](#)]

48. Bryant, D.A.; Canniffe, D.P. How nature designs light-harvesting antenna systems: Design principles and functional realization in chlorophototrophic prokaryotes. *J. Phys. B At. Mol. Opt. Phys.* **2018**, *51*, 0330011. [[CrossRef](#)]
49. Lokstein, H.; Renger, G.; Götze, J.P. Photosynthetic Light-Harvesting (Antenna) Complexes—Structures and Functions. *Molecules* **2021**, *26*, 3378. [[CrossRef](#)]
50. Köhler, J. Optical spectroscopy of individual light-harvesting complexes from purple bacteria. In *The Purple Phototrophic Bacteria*; Hunter, C.N., Daldal, F., Thurnauer, M.C., Beatty, J.T., Eds.; Springer: Dordrecht, The Netherlands, 2008; pp. 877–894.
51. Günther, L.M.; Knoester, J.; Köhler, J. Limitations of Linear Dichroism Spectroscopy for Elucidating Structural Issues of Light-Harvesting Aggregates in Chlorosomes. *Molecules* **2021**, *26*, 899. [[CrossRef](#)]
52. Demmig-Adams, B.; Stewart, J.J.; López-Pozo, M.; Polutchko, S.K.; Adams, W.W. Zeaxanthin, a Molecule for Photoprotection in Many Different Environments. *Molecules* **2020**, *25*, 5825. [[CrossRef](#)]
53. Makhneva, Z.K.; Bolshakov, M.A.; Moskalenko, A.A. Carotenoids Do Not Protect Bacteriochlorophylls in Isolated Light-Harvesting LH2 Complexes of Photosynthetic Bacteria from Destructive Interactions with Singlet Oxygen. *Molecules* **2021**, *26*, 5120. [[CrossRef](#)]
54. AWang, P.; Grimm, B. Connecting Chlorophyll Metabolism with Accumulation of the Photosynthetic Apparatus. *Trends Plant Sci.* **2021**, *26*, 484–495.
55. Kräutler, B. Breakdown of Chlorophyll in Higher Plants—Phyllobilins as Abundant, Yet Hardly Visible Signs of Ripening, Senescence, and Cell Death. *Angew. Chem. Int. Ed.* **2016**, *55*, 4882–4907. [[CrossRef](#)] [[PubMed](#)]
56. Cartaxana, P.; Rey, F.; LeKieffre, C.; Lopes, D.; Hubas, C.; Spangenberg, J.E.; Escrig, S.; Jesus, B.; Calado, G.; Domingues, R.; et al. Photosynthesis from stolen chloroplasts can support sea slug reproductive fitness. *Proc. R. Soc. B Biol. Sci.* **2021**, *288*, 1779. [[CrossRef](#)] [[PubMed](#)]
57. De Vries, J.; Christa, G.; Gould, S.B. Plastid survival in the cytosol of animal cells. *Trends Plant Sci.* **2014**, *19*, 347. [[CrossRef](#)] [[PubMed](#)]
58. Perez-galvez, A.; Viera, I.; Benito, I.; Roca, M. HPLC-hrTOF-MS study of copper chlorophylls: Composition of food colorants and biochemistry after ingestion. *Food Chem.* **2020**, *321*, 126721. [[CrossRef](#)] [[PubMed](#)]
59. Zhong, S.; Bird, A.; Kopec, R.E. The Metabolism and Potential Bioactivity of Chlorophyll and Metallo-chlorophyll Derivatives in the Gastrointestinal Tract. *Mol. Nutr. Food Res.* **2021**, *65*, 2000761. [[CrossRef](#)] [[PubMed](#)]
60. Szafraniec, M.J.; Fiedor, L. One ring is not enough to rule them all. Albumin-dependent ABCG2-mediated transport of chlorophyll-derived photosensitizers. *Eur. J. Pharm. Sci.* **2021**, *167*, 106001. [[CrossRef](#)]
61. Kashiyama, Y.; Yokoyama, A.; Kinoshita, Y.; Shoji, S.; Miyashita, H.; Shiratori, T.; Suga, H.; Ishikawa, K.; Ishikawa, A.; Inouye, I.; et al. Ubiquity and quantitative significance of detoxification catabolism of chlorophyll associated with protistan herbivory. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 17328–17335. [[CrossRef](#)]
62. Scheer, H.; Katz, J.J. New type of metalcomplexes related to chlorophyll. *J. Am. Chem. Soc.* **1975**, *97*, 3273–3275. [[CrossRef](#)]
63. Kinoshita, Y.; Demise, A.; Ishikawa, H.; Tamiaki, H. Synthesis of 132,173-cyclophorbides and their optical properties. *J. Photochem. Photobiol. A* **2021**, *420*, 113490. [[CrossRef](#)]
64. Porra, R.J.; Scheer, H. Towards a more accurate future for chlorophyll a and b determinations: The inaccuracies of Daniel Arnon's assay. *Photosynth. Res.* **2019**, *140*, 215–219. [[CrossRef](#)] [[PubMed](#)]
65. Esteban, R.; García-Plazaola, J.I.; Hernández, A.; Fernández-Marín, B. On the recalcitrant use of Arnon's method for chlorophyll determination. *New Phytol.* **2018**, *217*, 474–476. [[CrossRef](#)] [[PubMed](#)]
66. Lichtenthaler, H.K. Multi-colour fluorescence imaging of photosynthetic activity and plant stress. *Photosynthetica* **2021**, *59*, 364–380. [[CrossRef](#)]
67. Herppich, W.B. Chlorophyll fluorescence imaging for process optimisation in horticulture and fresh food production. *Photosynthetica* **2021**, *59*, 422–437. [[CrossRef](#)]
68. Valcke, R. Can chlorophyll fluorescence imaging make the invisible visible? *Photosynthetica* **2021**, *59*, 381–398. [[CrossRef](#)]
69. Porcar-Castell, A.; Malenovsky, Z.; Magney, T.; Van Wittenberghe, S.; Fernandez-Marin, B.; Maignan, F.; Zhang, Y.; Maseyk, K.; Atherton, J.; Albert, L.P.; et al. Chlorophyll a fluorescence illuminates a path connecting plant molecular biology to Earth-system science. *Nat. Plants* **2021**, *7*, 998–1009. [[CrossRef](#)]
70. Hikosaka, K.; Tsujimoto, K. Linking remote sensing parameters to CO₂ assimilation rates at a leaf scale. *J. Plant Res.* **2021**, *134*, 695–711. [[CrossRef](#)]
71. Noda, H.M.; Muraoka, H.; Nasahara, K.N. Plant ecophysiological processes in spectral profiles: Perspective from a deciduous broadleaf forest. *J. Plant Res.* **2021**, *134*, 737–751. [[CrossRef](#)]
72. Schreiber, U.; Klughammer, C. Evidence for variable chlorophyll fluorescence of photosystem I in vivo. *Photosynth. Res.* **2021**, *149*, 213–231. [[CrossRef](#)]
73. Chand, B.; Priyamvda; Kumar, M.; Prasher, S.; Kumar, M. Feasibility study of a chlorophyll dosimeter for high energy X-ray beam used in radiotherapy. *J. Radioanal. Nucl. Chem.* **2021**, *1–7*. [[CrossRef](#)]
74. Suvorov, N.; Pogorilyy, V.; Diachkova, E.; Vasil'ev, Y.; Mironov, A.; Grin, M. Derivatives of natural chlorophylls as agents for antimicrobial photodynamic therapy. *Int. J. Mol. Sci.* **2021**, *22*, 6392. [[CrossRef](#)] [[PubMed](#)]
75. Weishaupt, K.R.; Gomer, C.J.; Dougherty, T.J. Identification of singlet oxygen as the cytotoxic agent in photoinactivation of a murine tumor. *Cancer Res.* **1976**, *36*, 2326–2329. [[PubMed](#)]
76. Sternberg, E.D.; Dolphin, D.; Bruckner, C. Porphyrin-based photosensitizers for use in photodynamic therapy. *Tetrahedron* **1998**, *54*, 4151–4202. [[CrossRef](#)]

77. Staron, J.; Boron, B.E.; Karcz, D.; Szczygiel, M.; Fiedor, L. Recent Progress in Chemical Modifications of Chlorophylls and Bacteriochlorophylls for the Applications in Photodynamic Therapy. *Curr. Med. Chem.* **2015**, *22*, 3054–3074. [[CrossRef](#)] [[PubMed](#)]
78. Brandis, A.; Salomon, Y.; Scherz, A. Bacteriochlorophyll sensitizers in photodynamic therapy. In *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications*; Grimm, B., Porra, R., Rüdiger, W., Scheer, H., Eds.; Springer: Dordrecht, The Netherlands, 2006; pp. 485–494.
79. Sjoberg, H.T.; Philippou, Y.; Magnussen, A.L.; Tullis, I.D.C.; Bridges, E.; Chatrian, A.; Lefebvre, J.; Tam, K.H.; Murphy, E.A.; Rittscher, J.; et al. Tumor irradiation combined with vascular-targeted photodynamic therapy enhances antitumor effects in pre-clinical prostate cancer. *Br. J. Cancer* **2021**, *125*, 534–546. [[CrossRef](#)] [[PubMed](#)]
80. Brekelmans, J.; Dickman, M.M.; Verma, S.; Arba-Mosquera, S.; Goldschmidt, R.; Goz, A.; Brandis, A.; Berendschot, T.T.J.M.; Saelens, I.E.Y.; Marcovich, A.L.; et al. Excimer laser-assisted corneal epithelial pattern ablation for corneal cross-linking. *Acta Ophthalmol.* **2021**. [[CrossRef](#)] [[PubMed](#)]
81. Morozova, N.; Pavlova, M.; Plyutinskaya, A.; Pankratov, A.; Efendiev, K.; Semkina, A.; Pritmov, D.; Mironov, A.; Panchenko, P.; Fedorova, O. Photodiagnosis and photodynamic effects of bacteriochlorin-naphthalimide conjugates on tumor cells and mouse model. *J. Photochem. Photobiol. B* **2021**, *223*, 112294. [[CrossRef](#)]
82. Janik-Zabrotowicz, E.; Arczewska, M.; Prochniewicz, P.; Swietlicka, I.; Terpiłowski, K. Stability of Chlorophyll a Monomer Incorporated into Cremophor EL Nano-Micelles under Dark and Moderate Light Conditions. *Molecules* **2020**, *25*, 5059. [[CrossRef](#)]
83. Pinto, S.; Almeida, S.; Tomé, V.; Prata, A.J.F.; Calvete, M.; Serpa, C.; Pereira, M. Water soluble near infrared dyes based on PEGylated-Tetrapyrrolic macrocycles. *Dyes Pigments* **2021**, *195*, 109677. [[CrossRef](#)]
84. Sulaiman, L.; Abidin, Z.H.Z.; Yunus, S.A.M.; Mazni, N.A.; Hadi, A.N.; Arof, A.K.; Simarani, K. Dual functions of Cu(NO₃)₂ as antifungal and colour stabilizer for coating paint film consisting of chlorophyll. *Pigment. Resin. Technol.* **2021**, *50*, 177. [[CrossRef](#)]
85. Nouri, E.; Abbasi, H.; Rahimi, E. Effects of processing on stability of water- and fat-soluble vitamins, pigments (C-phycoerythrin, carotenoids, chlorophylls) and colour characteristics of *Spirulina platensis*. *Qual. Assur. Saf. Crops Foods* **2018**, *10*, 335. [[CrossRef](#)]
86. Duan, S.; Zhou, Q.; Li, A.; Wang, X.-F.; Sasaki, S.-I.; Tamiaki, H. Semisynthetic Chlorophyll Derivatives Toward Solar Energy Applications. *Sol. RRL* **2020**, *4*, 2000162. [[CrossRef](#)]
87. Stojanovic, M.; Flores-Diaz, N.; Ren, Y.; Vlachopoulos, N.; Pfeifer, L.; Shen, Z.; Liu, Y.; Zakeeruddin, S.M.; Milic, J.V.; Hagfeldt, A. The Rise of Dye-Sensitized Solar Cells: From Molecular Photovoltaics to Emerging Solid-State Photovoltaic Technologies. *Helv. Chim. Acta* **2021**, *104*, e2000230. [[CrossRef](#)]
88. Anonymous. The Chemical Record Lectureship for Michael Graetzel/Baizer Award for Flavio Maran/And also in the News. *Angew. Chem. Int. Ed.* **2018**, *57*, 877.
89. Kathpalia, R.; Verma, A.K. Bio-inspired nanoparticles for artificial photosynthesis. *Mater. Today Proc.* **2021**, *45*, 3825–3832. [[CrossRef](#)]