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A New Factor in Life's Quest for Energy**

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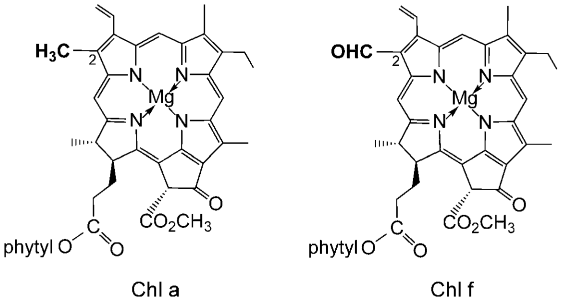
How life evolved on Earth, how it adapted from its earliest beginnings, and what global and local environmental conditions and chemical prerequisites were helpful in its genesis are most intriguing scientific questions (see, for example, reference [1]). Porphyrinoids, which are thought to be of prebiotic origin, may have played a critical role in this early development of life.[2,3] These tetrapyrroles possess basic structures that have proved to be remarkably useful in meeting a range of essential biological needs.[3–5]

Some of the best-documented early forms of life continue to be unearthed in paleobotanical studies, which suggest its beginnings to go back far beyond 3×10^9 years (early Precambrium).[6] A generally accepted scenario infers a "reducing" early environment, in which archaic anaerobic life forms developed a capacity to harness chemical energy in order to drive cellular life (see, for example, reference [7]).[7] Soon—in a geological sense—early photosynthetic organisms evolved and eventually caused a global environmental disaster: according to a widely held view, the oxygen-generating photosynthesis of cyanobacteria[6] led to the accumulation of oxygen and a switch of the environment from predominantly reducing to oxidizing.[8] This shift to an oxidizing atmosphere made most parts of the Earth uninhabitable for anaerobes. However, it also opened up a new opportunity for the biosphere and provided a foundation for the evolution of higher forms of life.[6]

Photosynthesis has driven the development of life, powered by the efficient capture and conversion of sunlight. The utilization of solar energy has thus become a cornerstone of evolution. In this context the ability to optimally absorb and harness sunlight and to adapt to the environmental (local, seasonal) conditions is critical. The partially reduced porphyrinoids broadly grouped as "chlorophylls" are thought to have played a major role.[4] Indeed, they eventually assumed a central position among the "pigments of life" and are considered the "most visual sign of life" on Earth.[4,9] Their biochemical functions depend, largely, on their well-adaptable optoelectronic properties.

A remarkable chlorophyll with unprecedentedly red-shifted absorption bands was recently discovered by an Australian–German research consortium.[10] This chlorophyll derivative was named Chlorophyll f (Chl f; Scheme 1)[10] to distinguish it from the other "chlorophylls", listed as Chlorophylls a–e (Chl a–e). Chl f was discovered in stromatolites from Shark Bay, Western Australia, which provide a unique environment for diverse cyanobacterial communities.[6,11] Chl f appears to originate from a specific filamentous cyanobacterium, which contains only Chl a and Chl f, and which could be cultured under near-infrared light (720 nm).[10]



Scheme 1. Structural formulae of chlorophyll a (Chl a)[5] and chlorophyll f (Chl f).[10]

Compared to porphyrins, the chromophores of the dihydroporphyrinoid chlorophylls (Chls) and—even more dramatically—of the tetrahydroporphyrinoid bacteriochlorophylls (BChls, for example, BChl a) display a spectacular shift and intensification of absorbance bands in the long-wavelength part of the visible spectrum or in the near-infrared (see Figure 1). This shift to longer wavelengths is mostly caused by a minor reduction in the size and symmetry of the conjugated porphyrinoid π system.[4] Chls and BChls are, thus, much better (than porphyrins) at collecting a major part of the sunlight. How they were biosynthesized in the early biotic era is not known.[4c] In today's photosynthetic organisms the photoactive chromophores of Chls and BChls are generated from a colorless tetrapyrrole (uroporphyrinogen III) by truly elaborate biosynthetic pathways.[4]

Photosynthetic organisms have learned to make use of every part of the structure of their photoactive chlorophylls. They have thus found ways to insert the crucial magnesium ions, and to further adapt and finetune Chls by additional minor modifications at the periphery of the macrocycle. An

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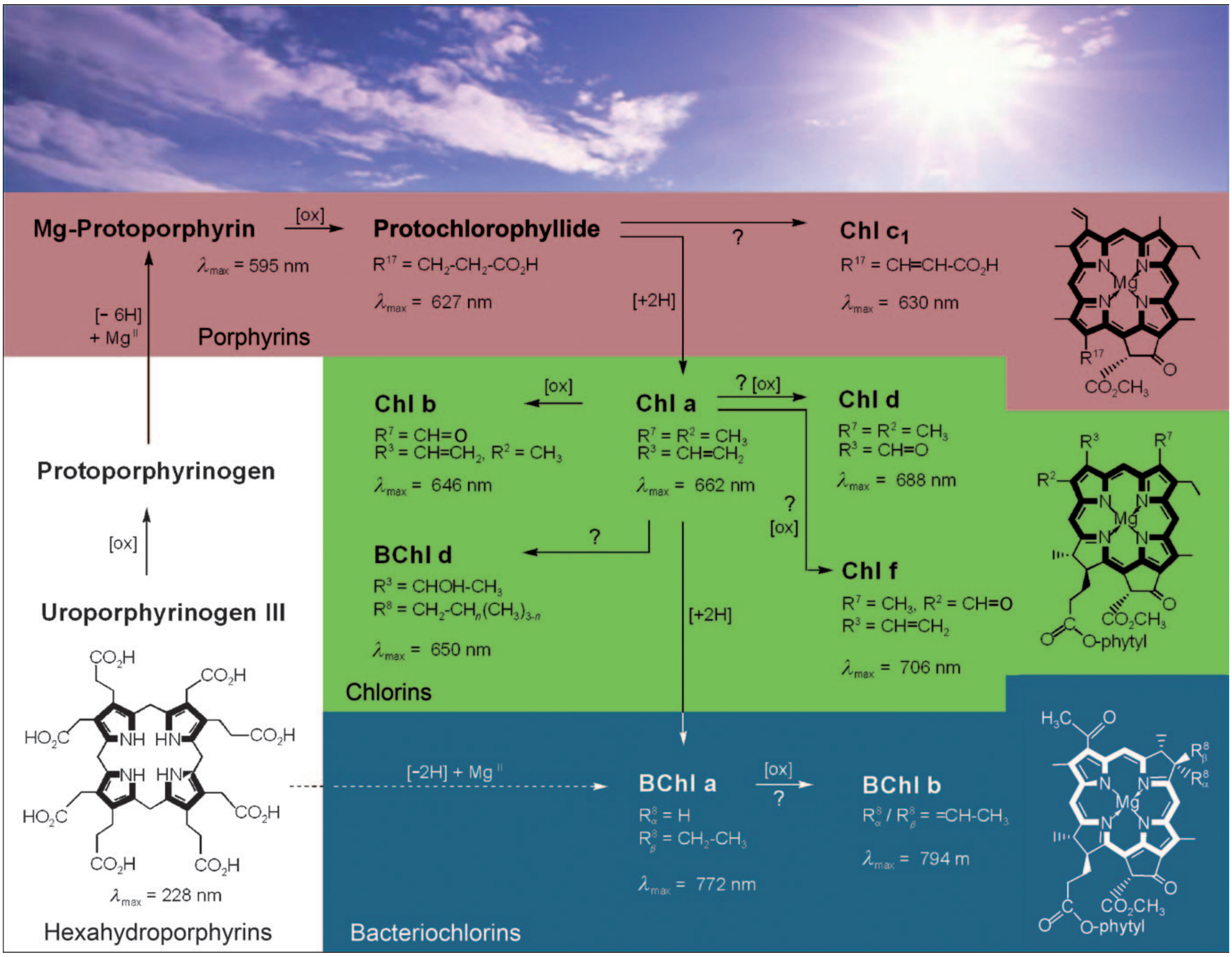

Figure 1. Overview of key porphyrinoid compounds relevant to photosynthesis and chlorophyll biosynthesis: the genuine Chls (Chl a, Chl b, Chl d, and Chl f), as well as BChl d absorb red light; they are 17,18-dihydroporphyrins (chlorines; green section) with absorption maxima near 650–700 nm. Genuine bacteriochlorophylls, like BChl a and BChl b, absorb sunlight in the near infrared; they are 7,8,17,18-tetrahydroporphyrins (bacterichlorins; dark blue section) with absorption maxima near 770–800 nm. Chl c, protochlorophyllide, and Mg-protoporphyrin are porphyrins that show absorption maxima near 600–630 nm. Formal saturation (or desaturation) processes of core sections of the porphyrinoid chromophore are symbolized with [+ *n*H] and [−*n*H], respectively; formal oxidative transformations in the periphery is represented by [ox]; a dashed arrow indicates a formal structural correlation.

established example in this respect is the modification of Chl a to Chl b by (enzyme-catalyzed) oxidation of the methyl group at C7 to a formyl group,[4d] which causes the absorbance maximum at longest wavelength to undergo a hypsochromic shift by 16 nm (see Figure 1).[4b] A similarly effective, but bathochromic effect by 26 nm is found in Chl d, in which C3 carries a formyl group.[4b] An even more dramatic bathochromic shift of the absorbance maximum results from assembly of Chls into "special pairs" in the photoreaction centers.[12] The biological relevance of most of these structural variations can be rationalized by the optimization of the absorption of sunlight and for its efficient use through the generation of a charge-separated primary product in the living cell. Recent studies have provided synthetic models of Chl b and Chl d, confirming that the carbonyl groups at C3, C7, and C13 are relevant factors in providing Chls with their specific photochemical properties.[13]

The sample of Chl f isolated by Chen et al. was purified by repeated HPLC and characterized by UV/Vis and ^{1}H NMR spectroscopy, as well as by mass spectrometry.[10] A solution of Chl f in methanol exhibited a record shift of its absorbance maximum at the longest wavelength to 706 nm, and its fluorescence was observed at 722 nm. The maxima are thus shifted to a longer wavelength by over 40 nm relative to those of Chl a.[10] Based on an ion signal at m/z 906.218 in the MALDI-TOF mass spectrum, the molecular formula was deduced as $C_{55}H_{70}N_4O_6Mg$, and its fragment at m/z 628.092 (loss of $C_{20}H_{40}$) was taken to indicate a phytyl unit. The presence of the new formyl group at C2 was deduced from a singlet at low field in the ^{1}H NMR spectrum and from the position of three more (methine) singlets (all supported by comparison of experimental and calculated chemical-shift values). The multiplet of a vinyl group was also identified and assigned tentatively. The suggested new chromophore of Chl f was further tested by density functional (DFT) calculations of the optical spectra,[10] which also made several other substitution patterns highly unlikely. The reported experimental and calculated values thus provide good evidence for the basic features of the proposed chromophore of Chl f. The latter would only differ from Chl a by the replacement of a methyl by a formyl group at C2 (see Scheme 1). Further studies are required to completely secure the molecular constitution and the stereochemical aspects of the proposed structure of Chl f.

Detailed 2D NMR spectroscopic investigations of Chl f and/or synthetic work (see, for example, reference [13]) may be helpful in testing its proposed structure and in clarifying those sections for which actual structural information is still unavailable. The functional role of Chl f in the cyanobacterium and its biosynthesis are two other intriguing topics to be studied. Clearly, the bathochromic shift of the absorption bands increases the amount of sunlight absorbed in the near infrared. This may suggest a role of Chl f in the collection of sunlight. The modern marine stromatolites in which Chl f was discovered are built-up by the mineralization of colonies of diverse microorganisms,[11] which are dominated by photosynthetic cyanobacteria. Quite likely, the new chromophore is a further result of the biological adaptation and optimization of the cyanobacteria in their struggle for survival, and a sign of life's constant demand for energy captured from sunlight by means of photosynthesis.

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