A near-infrared light photosynthetic pigment

Ujjal Kumar Sur

Chlorophyll is a green pigment found in almost all plants, algae and cyanobacteria. Its name is derived from the Greek words *chloros* meaning green and *phyllon* meaning leaf. Chlorophyll absorbs light most strongly in the blue portion of the electromagnetic spectrum, followed by the red portion. However, it is a poor absorber of green and near-green portions of the spectrum, hence the green colour of chlorophyll-containing tissues. Chlorophyll was first isolated by Joseph Bienaimé Caventou and Pierre Joseph Pelletier in 1817. It is vital for photosynthesis, for which it harvests solar energy and transduces it into chemical energy. In this process, the energy absorbed by chlorophyll transforms carbon dioxide and water into carbohydrates and oxygen:

$$CO_2 + H_2O \rightarrow (CH_2O) + O_2.$$

There are four chemically distinct varieties of chlorophylls known for the last 60 years in oxygenic photosynthetic organisms. They are termed as Chl *a*, *b*, *c* and *d* in the order of their discovery[1].

The two currently accepted photosystem units are Photosystem II and Photosystem I, which have their distinct reaction centre chlorophylls, named P680 and P700 respectively. These pigments are named after the wavelength (in nanometers) of their red-peak absorption maximum. The identity, function and spectral properties of the types of chlorophyll in each photosystem are distinct and determined by each other and the protein structure surrounding them. Chlorophyll has essentially two parts: a substituted porphyrin ring and phytol (the long carbon chain). The porphyrin ring is an excellent chelating ligand, with the four nitrogen atoms binding strongly to a co-ordinated metal atom in a square planar arrangement. It contains magnesium (Mg^{2+}) ion at the centre of the porphyrin ring. Figure 1 illustrates the chemical structures of Chl *a* and *b* and Figure 2 illustrates the chemical structure of Chl *c* and *d*. All the four pigments are present in light-harvesting complexes. Until recently, only Chl *a* was thought to be responsible for energy transduction in the photosynthetic systems[2]. This concept was challenged by the discovery of Chl *d* in 1943 (ref. 3). Chl *d* was shown to constitute up to 99% of all chlorophyll in the cyanobacterium *Acaryochloris marina*[4]. In this organism, Chl *d* can replace Chl *a* in the photosystems of oxygenic photosynthesis. It can absorb the red portion of sunlight, which can be harvested for carbon fixation[5].

A new type of chlorophyll has been discovered and studied by a team of

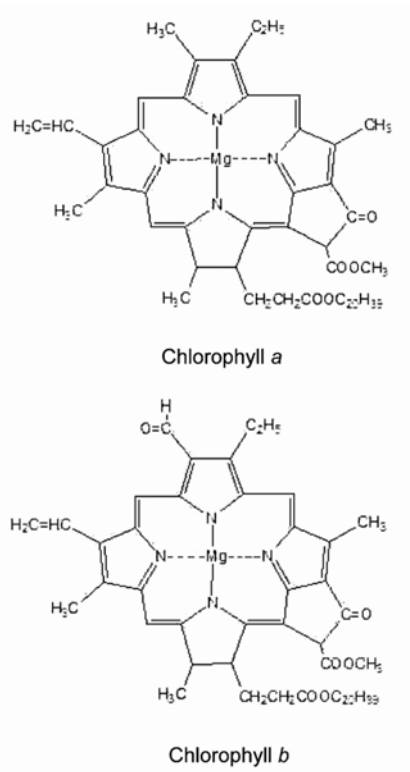


Figure 1. Chemical structures of Chl *a* and *b*.

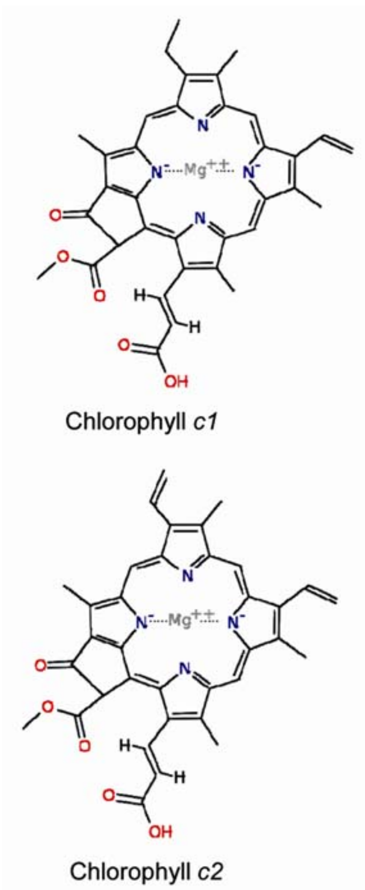


Figure 2. Chemical structures of Chl *c* and *d*.

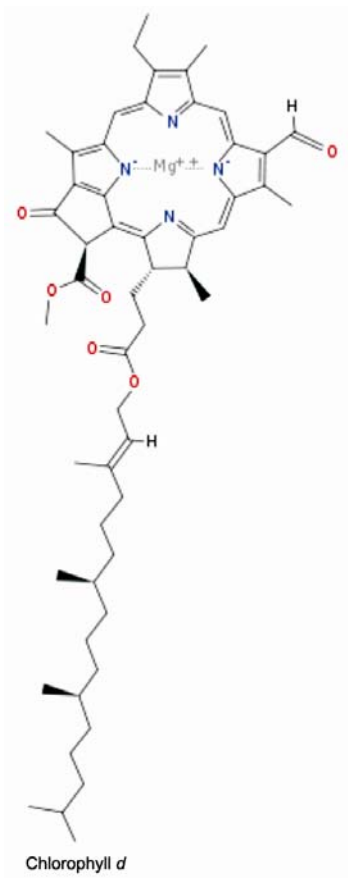


Figure 3. Chemical structure of Chl *f* with comparison to other chlorophylls. (From Chen *et al.*[6], reprinted with permission from *AAAS*.)

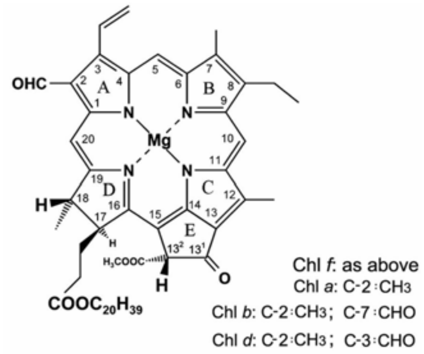
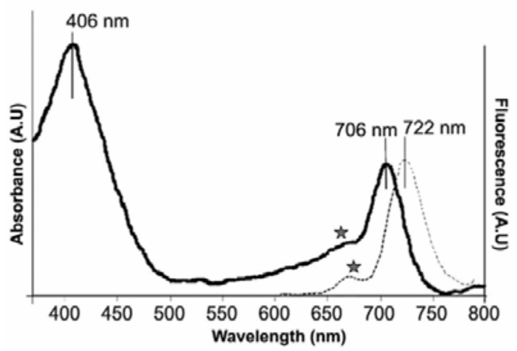


Figure 4. Absorption and fluorescence emission spectra of purified Chl *f* in methanol at room temperature. (From Chen *et al.*[6], reprinted with permission from *AAAS*.)



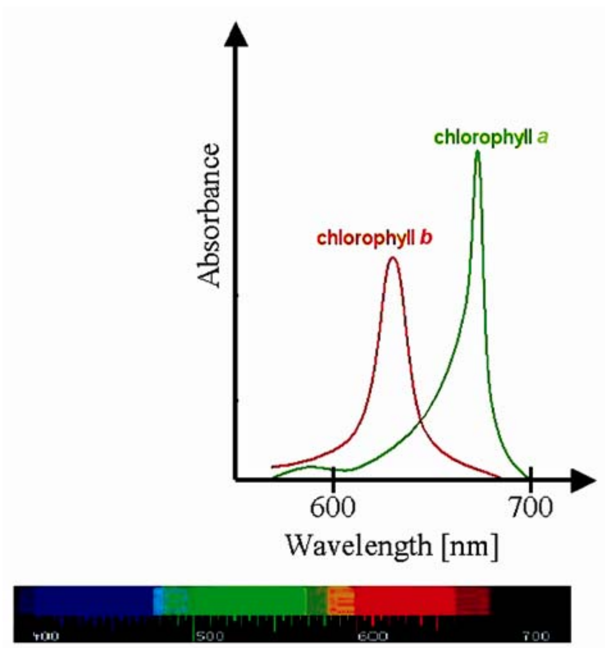


Figure 5. Absorbance spectra of free chlorophyll *a* (green) and *b* (red) in a solvent.

researchers led by Min Chen of the University of Sydney, Australia[6]. This new type of chlorophyll is known as chlorophyll *f*, the researchers cultured it from dense mats of cyanobacteria called stromatolites that are among the oldest surviving biological communities on Earth. Figure 3 shows the chemical structure of Chl *f* with comparison to other chlorophylls.

Illuminating the cells with infrared light allowed the researchers to obtain cultures with a high concentration of organisms containing the novel Chl *f*. Analysis of the chlorophyll showed that it is structurally similar to Chl *a* but can absorb infrared light at lower wavelengths than any of the four known types of chlorophyll. Its *in vitro* absorption and fluorescence maxima are 706 nm and 722 nm respectively. Figure 4 shows the absorption and fluorescence emission spectra of purified Chl *f* in methanol at room temperature. Figure 5 illustrates absorbance spectra of free Chl *a* (green) and *b* (red) in a solvent. Based on nuclear magnetic resonance data, optical and mass spectra, it is thought to have a structure of $C_{55}H_{70}O_6N_4Mg$ or [2-formyl]-chlorophyll *a*. The research might make it possible to modify the absorption spectra of other chlorophylls and could facilitate novel technical or biohybrid systems that convert sunlight into energy. This finding suggests that oxygenic photosynthesis can be extended further into the infrared region of the electromagnetic spectrum and may open associated bioenergy applications.

The researchers believe that a formyl group at a specific position in the molecule causes the red shift in the absorption spectrum and say that Chl *f* is the first new chlorophyll found in oxygenic phototrophs in over 60 years.

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Ujjal Kumar Sur is in the Department of Chemistry, Behala College, Kolkata 700 060, India.
e-mail: uksur99@yahoo.co.in