THE DIVERSITY OF PHOTOSYNTHETIC PIGMENTS. Robert E. Blankenship, Departments of Biology and Chemistry, Washington University in St. Louis, St. Louis, MO 63130 USA. Blankenship@wustl.edu.

Introduction: Photosynthetic organisms contain a bewildering array of light-absorbing pigments. In chlorophyll-based photosynthesis these pigments function as both an antenna, increasing the capture cross section of the organism for electromagnetic radiation and also as a photochemically active pigment that carries out electron transfer chemistry. They also provide photoprotection.

The three types of pigments that participate in photosynthetic energy conversion are chlorophylls, carotenoids and bilins. Chlorophylls are cyclic tetrapyrrole molecules, carotenoids are linear polyenes and bilins are open chain tetrapyrroles [1].

Chlorophylls can be more accurately described chemically as porphyrins (Chl *c*), chlorins (Chl *a, b, d, f* and BChl *c, d, e*) or bacteriochlorins (BChl *a, b, g*), depending on whether they have 0, 1 or 2 of the pyrrole rings reduced in the macrocycle. The electronic transitions that give chlorophylls their characteristic color are π to π^* transitions in which the π electrons are redistributed upon absorption of a photon of the appropriate energy. There are two major electronic transitions in most chlorophylls, the long wavelength Q band in the red region of the visible spectrum and the B band in the blue region of the spectrum. In most cases, chlorophylls are associated with proteins at very specific binding sites. The absorption maxima depend on the polarity of the solvent and interactions with cellular proteins *in vivo*.

Carotenoids typically have from X to Y conjugated double bonds in the linear polyene backbone and typically absorb in the 400-500 nm spectral range. Bilins are in most cases covalently linked to proteins via thioether linkages, and absorb in the 550-650 nm range. Both carotenoids and bilins function as antenna pigments, absorbing energy and transferring it to chlorophylls, where it is used to do photochemistry. Carotenoids also function in photoprotection and regulation of energy flow.

Recently, there has been considerable interest in the possibility of photosynthesis on extrasolar planets around K or M class stars, where the longer wavelength stellar emission does not match well with the pigments that are found on Earth-based organisms [2]. However, some chlorophylls are significantly red-shifted to adapt the organisms that contain them to filtered light environments that are substantially depleted in visible light. These include in particular Chl *d* and *f*, which are found in cyanobacteria that occupy such environments. These pigments extend the range of Photosynthetically Active Radiation (PAR) out to 750 nm from the traditional limit of 700 nm. These pigments are found in certain cyanobacteria that can carry out oxygenic photosynthesis driven by light up to 750 nm [3,4]. Other organisms can carry out anoxygenic photosynthesis using light with wavelengths that extend to 1000 nm.

The known pigments that can drive photosynthesis on Earth are not the only possible pigments that can potentially drive light-energy capture mechanisms. A remarkable range of organic molecules can potentially serve as photopigments, in that they have sufficiently strong molecular absorbance and long excited state lifetimes so that the energy can be harvested by photochemistry. Other cellular architectures that could possibly extend chlorophyll-based photosynthesis into the longer wavelength region include three or more photosystems acting in series [5], in contrast to the two photosystem architecture of oxygenic photosynthesis and the one photosystem architecture of anoxygenic photosynthesis [1]. Other possibilities include metal-based systems such as ruthenium complexes that have been employed for artificial photosynthesis but have not been found in any organism on Earth.

In addition to chlorophyll-based photosynthesis, there are a number of bacteria and archaea that utilize a retinal-based type of photosynthesis that pumps protons across a membrane rather than transferring electrons [6]. These organisms are very widely distributed, but none of them has been shown to be able to carry out photoautotrophic metabolism, where they derive all their cellular energy requirements from this mechanism.

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